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THE DECOMPOSITION POTENTIALS OF COORDINATION COMPOUNDS OF ALUMINUM BROMIDE IN THE MOLTEN STATE*

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The electrochemical investigations of V.A.Plotnikov and his associates [1] on ternary systems consisting of aluminum bromide, halides of metals of Groups I and V of the periodic system, and an organic solvent have shown that for benzene, toluene, xylene, ethyl bromide, and ethylene bromide solutions of aluminum bromide and the halide of the alkali metal, the decomposition potential of these systems is close to the decomposition potential of aluminum bromide. Metallic aluminum is deposited on the cathode during the electrolysis of these systems. When solutions of $AlBr_3$ (in an organic solvent), which also contain halides of a metal of Group V of the periodic system, either copper or silver, are electrolyzed, the corresponding metal is deposited on the cathode, depending on the composition of the system.

Nitrobenzene [2] and nitromethane [3] solutions of aluminum bromide and halides of the alkali metals behave quite differently. When these solutions are electrolyzed, the alkali metal is deposited on the cathode, no matter what the concentrations of the components of the system.

Ya. P. Mezhenny [4], in a study of the decomposition potentials of lithium or sodium chloride in an ethyl bromide solution of aluminum bromide, discovered that the decomposition potentials of the above halides of the alkali metals exist, in addition to the decomposition potential of $AlBr_3$.

The systematic researches of S.I. Yakubson [5] on the decomposition potentials of ternary systems – halides of the alkali metals, aluminum bromide, and various organic solvents – as functions of the concentration of the constituents have shown that when the molecular ratio of the MeHd (MeLi, Na, K) to the $AlBr_3$ ranges from 0.3 to 0.6, only one inflection is found in the I – V curve, corresponding to the decomposition potential of aluminum bromide. As the concentration of the alkali metal halide is increased still further, i.e., starting with a molecular ratio of the MeHd to $AlBr_3$ of from 0.6 to 1, there are two inflexions on the I – V curve, the second one representing the alkali metal halide. With equimolecular ratios of these salts, only the second potential is present, corresponding to the decomposition potential of the alkali metal halide.

S.I.Yakubson and M.A.Abramov [6] established the existence of two decomposition potentials for LiHd – $AlBr_3$ solutions in benzene, toluene, and ethylene bromide, the first corresponding to the deposition of aluminum, and the second to

*This research was completed before the war (in 1940), and had to be reprated because of its loss during the invasion of the Ukraine by German fascist bands.

lithium.

Thus, the electrolytic deposition of the alkali metals from the foregoing ternary systems containing ethyl bromide, ethylene bromide, benzene, or toluene is governed by the molecular ratio of the alkali metal halides to the aluminum bromide, while one can always deposit the alkali metal from the nitrobenzene solutions of the same salts, no matter what their molecular ratio.

Investigation of the effect of nitrobenzene upon the decomposition potential of the ternary system KBr – $AlBr_3$ – C_2H_5Br [7] indicated that though the decomposition potential was 1.95 volts when no nitrobenzene was present, corresponding to the decomposition potential of aluminum bromide, the decomposition potential rose to 4.38 volts when a small amount of $C_6H_5NO_2$ was added, corresponding to the decomposition potential of the alkali metal. Any further increase in the percentage of nitrobenzene has but little effect upon the size of the decomposition potential.

Adding benzene to the ternary system KBr – $AlBr_3$ – $C_6H_5NO_2$ causes no change in the value of the decomposition potential [8], which corresponds to the decomposition potential of the alkali metal.

V. A. Izbekov has investigated the decomposition potentials of various metal bromides in $AlBr_3$ as a solvent [9], finding that the decomposition potential equaled 1.6 volts, corresponding to the deposition of aluminum, in the systems NaBr – $AlBr_3$ and KBr – $AlBr_3$.

Ya. P. Mezhenny has measured the decomposition potential in the systems LiCl – $AlBr_3$, NaCl – $AlBr_3$, and KCl – $AlBr_3$ in the molten state. This author found that aluminum is deposited at the cathode when these systems are electrolyzed, the decomposition potential being 1.62 volts for the first system, and being the same as that obtained by V. A. Izbekov [9] for the NaBr – $AlBr_3$ and KBr – $AlBr_3$ systems.

It follows from the foregoing that the magnitude of the decomposition potential and the deposition of one metal or another during electrolysis depend upon the nature and the composition of the coordination compound formed in the solution.

Thermal analysis was employed to prove that several metal bromides form coordination compounds with $AlBr_3$ of the following composition: $MeBr \cdot Al_2Br_6$ and $MeBr \cdot AlBr_3$ [11].

In the systems listed above, with ethylene bromide, ethyl bromide, benzene, or toluene, two decomposition potentials are found to exist when the molecular ratio of the MeHd to $AlBr_3$ > 0.5-0.6, corresponding to the formula $MeHd \cdot Al_2Br_6$, one decomposition potential being present, corresponding to the decomposition potential of the alkali metal, when the MeHd and the $AlBr_3$ are present in an equimolecular ratio. We were naturally interested in exploring the decomposition potentials of the coordination compounds of aluminum bromide, the composition of which had been established by thermal analysis with no solvent present, i.e., in the molten state, in order to check the existence of two potentials for coordination compounds that contain an alkali metal halide.

Initial Substances and Operational Methods

Aluminum bromide and antimony bromide were produced by the customary methods. The repeatedly distilled products were stored in sealed ampoules.

Zinc bromide was prepared by the method described in the paper by E.Ya. Gorenbein, [12].

Thallium bromide (TlBr) [13] was prepared from thallium acetate and hydrobromic acid. The precipitate of TlBr was carefully washed with water, dried, and stored in an exsiccator.

Lead bromide was prepared by reacting hydrobromic acid with lead oxide. The resulting $PbBr_2$ was recrystallized, dried, and stored like the TlBr.

The potassium bromide and chloride were purified by recrystallization, then dried and stored in an exsiccator.

Purified and recrystallized sodium bromide was calcined to drive off the water of crystallization. The anhydrous NaBr was stored in sealed ampoules.

Lithium chloride (C.P.) was dehydrated in a current of HCl. The anhydrous LiCl was stored like the NaBr.

We determined the decomposition potential from the I – V curves.

The vessel in which the melt was placed was fitted with platinum point electrodes sealed into glass tubes with well-ground stoppers.

For decomposition potentials up to 3 volts we used a voltmeter with a scale graduated in 0.02 volt, and used a voltmeter with a scale graduated to 0.1 volt for higher potentials – from 3 to 6 volts.

The current was measured with a milliammeter, accurate to 10^{-5} amp. We used a milliammeter with a scale reading in 0.05 and 0.5 amp for coordination compounds that contained an alkali metal.

We used an electric crucible furnace as a thermostat. The constancy of the temperature was checked by means of an ordinary thermometer.

The coordination compounds were prepared as follows.

First fused $AlBr_3$ was poured into a vessel with a ground-glass stopper and a lateral tube; after it solidified, the quantity of aluminum bromide was weighed, and a calculated amount of the appropriate metal halide was added, depending upon the composition of the coordinatien compound as fixed by thermal analysis [11]. The mixture was fused and carefully shaken, after which it was poured into ampoules with drawn-out necks, which were sealed at once.

There are no figures in the literature on the thermal analysis of the LiCl – $AlBr_3$ system, and we therefore prepared melts as we had for the KCl – $AlBr_3$ system, the constituents of which form two coordination compounds, $KCl \cdot Al_2Br_6$ and $KCl \cdot AlBr_3$, according to the thermal analysis [14].

The coordination compounds thus prepared were converted into the molten state in the vessel used for measuring the decomposition potentials. The vessel with its contents was placed in the thermostat, and measurements were made after the desired temperature had been established.

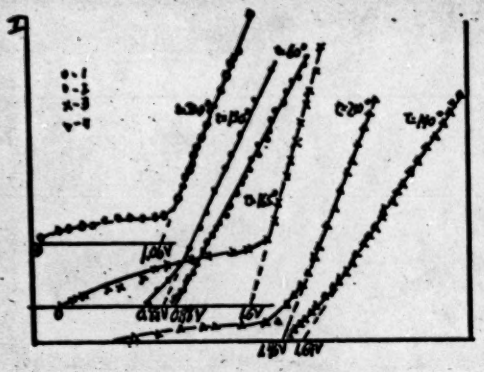
Test Results

The results of measurements of the coordination compounds $ZnBr_2 \cdot Al_2Br_6$, $PbBr_2 \cdot Al_2Br_6$, $TlBr \cdot Al_2Br_6$, and $SbBr_3 \cdot AlBr_3$ are shown in the figure.

The decomposition potential was 1.64 volts for the coordination compound $ZnBr_2 \cdot Al_2Br_6$ at 140° and 1.46 volts at 210°. It was 1.06 volts for $PbBr_2 \cdot Al_2Br_6$ at 300° and 1.6 volts for $TlBr \cdot Al_2Br_6$ at 165°. For $SbBr_3 \cdot AlBr_3$ the decomposition voltage was measured in the supercooled state (the melting point of the coordination compound is 82.5°); it was 0.98 and 0.96 volt at 60 and 80°, respectively. At 130° the decomposition potential was 0.88 volt. It is typical that the numerical values of the decomposition potential recorded by us differ only slightly from those obtained by V.A.Izbekov [15] for concentrations that did not correspond to the composition of the compounds. At 31.81% by weight of $ZnBr_2$, for instance, the decomposition potential was 1.56 volts at 100°, whereas it was 0.9 – 0.88 volt for $SbBr_3$ at the same temperature and at various concentrations (12-89% by weight). Apparently, the I – V curve method is not very sensitive, which is why the concentration does not exhibit much of an effect upon the magnitude of the decomposition potential. Moreover, it must be remembered that the

decomposition potentials measured by V.A.Izbekov also refer to coordination compounds of the composition mentioned above, even though $AlBr_3$ was present in excess.

The same convergence is found when we compare our results with those obtained by Yu. K. Delimarsky and V.A.Izbekov [16] in their measurements of the decomposition potentials of the same bromides in a melt of KBr + 3 $AlBr_3$ at 105°.



o – $PbBr_2 \cdot Al_2Br_6$, • – $SbBr_3 \cdot AlBr_3$,
x – $TlBr \cdot Al_2Br_6$, Δ – $ZnBr_2 \cdot Al_2Br_6$.

A considerable discrepancy is found to exist only with respect to the decomposition potential of $PbBr_2$. According to the foregoing authors, the decomposition potential of $PbBr_2$ in a melt of KBr + 3$AlBr_3$ is 1.48 volts, whereas we found that the decomposition potential of the coordination compound $PbBr_2 \cdot Al_2Br_6$ to be 1.06 volts at 300°. This discrepancy is apparently due to the presence of potassium bromide in the melt investigated by Yu.K.Delimarsky and V.A.Izbekov and to the difference in the test temperatures (105 and 300°).

An altogether different picture is observed for the decomposition potentials of coordination compounds of aluminum bromide containing alkali metal halides. All the decomposition potentials of MeHd – $AlBr_3$ systems in the molten state (Me = Li, Na, K) studied up to the present time have yielded a figure of 1.6 volts, with metallic aluminum deposited during electrolysis. Our research has shown that another potential may be obtained at a high current density, representing the potential of deposition of the alkali metals.

The results of our measurements of the decomposition potentials of coordination compounds that contain alkali metal halides are listed in Table 1.

TABLE 1

Coordination compound	Temperature	Decomposition potentials, volts	
		I	II
$LiCl \cdot Al_2Br_6$	120°	1.60	3.1
$LiCl \cdot AlBr_3$	200	1.80	3.2
$NaBr \cdot Al_2Br_6$	100	1.55	3.7-3.9
$NaBr \cdot AlBr_3$	230	1.80	3.7-4.8
$KBr \cdot Al_2Br_6$	200	1.56	
$KBr \cdot AlBr_3$	250	1.70	4.2
$KCl \cdot Al_2Br_6$	150	1.60	4.9
$KCl \cdot AlBr_3$	230	2.0	4.6

It was not always possible to measure the other potentials accurately, owing to the oscillations of the voltmeter pointer; moreover, allowance must be made for depolarization, caused by the interaction of of the electrolysis products with one another. Still, the values we obtained for the second potential indicate that this potential represents the deposition of the alkali metal. To check whether an alkali metal is deposited, we electrolyzed these coordination compounds at 6-8 volts. At the cathode we discovered the respective alkali metal, depending on the composition of the coordination compound, in addition to metallic aluminum.

Thus one can electrolytically deposit the alkali metal as well as the aluminum

from molten systems at high current densities. In this respect the electrochemical properties of these melts change but little when an organic solvent with a low dielectric constant (benzene, toluene, xylene, ethyl bromide, or ethylene bromide) is added.

The fact that the initial decomposition potentials of coordination compounds with an equimolecular composition, which contain alkali metal halides, is somewhat higher than those for coordination compounds containing two mols of $AlBr_3$ is worthy of note. This can apparently be explained by the differences in the heats of formation of these compounds.

It should be noted that the decomposition potentials of these coordination compounds are, as a rule, higher in various organic solvents than in the molten state. Differences in the concentrations and temperatures used in the tests can hardly affect the decomposition potentials to that extent. The discrepancy between the values of the first decomposition potentials of the coordination compounds we have examined in their molten state and in solution must be ascribed to the heats of formation of the more complex coordination compounds from the components of the system and the organic solvent.

SUMMARY

1. The decomposition potentials of the coordination compounds

$LiCl \cdot Al_2Br_6$, $LiCl \cdot AlBr_3$, $NaBr \cdot Al_2Br_6$,
$NaBr \cdot AlBr_3$, $KBr \cdot Al_2Br_6$, $KBr \cdot AlBr_3$,
$KCl \cdot Al_2Br_6$, $KCl \cdot AlBr_3$, $ZnBr_2 \cdot Al_2Br_6$,
$PbBr_2 \cdot Al_2Br_6$, $TlBr \cdot Al_2Br_6$, and $SbBr_3 \cdot AlBr_3$

have been measured in the molten state.

2. Two decomposition potentials have been found to exist in coordination compounds that contain alkali metal halides; the first potential represents the deposition of aluminum, while the second one corresponds to the alkali metal.

3. When molten coordination compounds that contain alkali metal halides are electrolyzed, the corresponding alkali metal is deposited at the cathode together with aluminum when the current density is high.

4. The decomposition potentials of the coordination compounds $ZnBr_2 \cdot Al_2Br_6$, $PbBr_2 \cdot Al_2Br_6$, and $SbBr_3 \cdot AlBr_3$ represent the deposition potential of the heavy metal.

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THE EFFECT OF SUBSTANCES THAT LOWER THE SURFACE TENSION UPON THE CATHODIC DEPOSITION OF CADMIUM

V. Sotnikova and M. Loshkarev

INTRODUCTION

The pronounced effect of the adsorption of neutral surface-active substances upon the kinetics of the cathodic deposition of tin, previously discovered by us [1], ought to be typical of many electrode reactions in some degree. In the present paper we make an endeavor to check this hypothesis.

The adsorption of ionic as well as of molecular surface-active substances to metals takes place within a restricted range of potentials. This condition is most sharply manifested for the additions of a molecular nature, which can form stable films only at fairly low charges on the electrode surface. In most instances a deviation of 0.4 to 0.7 volt to either side of the zero-charge potential (φ_0) results in their desorption. Thus, the possibility that chemical polarization of this type will occur is restricted by the requirement that the equilibrium potentials be rather close to the zero charge point of the surface. In many instances, however, the difference between these latter values is not very great. In Table 1 we have compared the values of the standard potentials for a number of electrode processes with the most probable values of the potentials of the zero point according to the data reported by Academician A.N.Frumkin at the 1947 session of the Division of Chemical Sciences of the USSR Academy of Sciences. As is shown in the table, it is possible for molecular adsorbed films to be formed in most of the processes listed.

We were therefore very much interested in tracing the action of the additives that had been found to be active upon the cathode process when other metals are deposited. We chose cadmium as the metal in question. The shift of the zero-charge point on the surface of Cd toward negative voltages compared to its standard potential made it seem likely that organic additives would result in high chemical polarization.

In the literature we find numerous references to the improvement of the structure of cathodic deposits of cadmium and zinc by adding colloid and surface-active substances to the electrolyte. K.M.Gorbunova [2], for example, noted that the nature of the growth of cadmium crystals changed when nicotine sulfate and brucine were added. The research work of Planer [3] as well as that done by Kudryavtsev, established the great improvement in the deposit caused by the use of commercial cadmium phenolsulfonate baths with a colloid. In the extensive literature of the past few years we also find recommendations that cresol- and naphtholsulfonic acids be added [4], as well as various condensation products of amines with aldehydes and ketones [5], furfural, various colloids [6], and other compounds.

TABLE 1

Comparison of Standard Potentials with Zero-Charge Surface Potentials

Metal	Electrode reaction	Standard potentials against a calomel electrode	Zero-charge surface potentials of the metal	
			With respect to the zero-charge potential of Hg	With respect to the standard calomel electrode
Pt	$Pt^{++} 2a \rightarrow Pt$	+0.920	+0.50	0.00
Ag	$Ag^{+} + e \rightarrow Ag$	+0.520	+0.27	−0.23
Hg	$Hg_2^{++} + 2e \rightarrow Hg$	+0.519	0.00	−0.50
Bi	$Bi^{++} + 3e \rightarrow Bi$	−0.066	−0.20	−0.70
Pb	$Pb^{++} + 2e \rightarrow Pb$	−0.407	−0.37	−0.87
Sn	$Sn^{++} + 2e \rightarrow Sn$	−0.416	−0.13	−0.63
		−0.416	−0.09	−0.59
Tl	$Tl^{+} + e \rightarrow Tl$	−0.616	−0.49	−0.99
		−0.616	−0.55	−1.05
Cd	$Cd^{++} + 2e \rightarrow Cd$	−0.682	−0.53	−1.06
Ga	$Ga^{+++} + 3e \rightarrow Ga$	−0.800	−0.40	−0.90
Zn	$Zn^{++} + 2e \rightarrow Zn$	−1.042	−0.45	−0.95

The decrease in the grain size and the increase in the density and uniformity of growth of cadmium deposits, noted by many authors, indicate the probability that the electrode processes are retarded by the addition of various organic compounds to the electrolyte.

In our research we confined our attention chiefly to a study of the effect of the group of active compounds, which we had already discovered to exist in the deposition of tin. The data cited above indicate that at least some of these compounds possess a notable retarding effect upon the electrode process we had chosen. At the same time, comparison of the differing effect of the same additives upon various processes provides us with additional experimental data characterizing the specific properties of each of the systems under investigation.

In its electrochemical behavior cadmium resembles tin. But when it is deposited from solutions of simple salts, considerable chemical polarization is observed [7], varying with the nature and concentration of the electrolyte. The influence of additions of surface-active substances in this case might be somewhat more complicated than in the case of tin.

In our research we used an electrolyte containing 0.25 N $CdSO_4$ and 0.05 N – 0.075 N H_2SO_4. The cadmium sulfate was subjected to double recrystallization. All our experiments were conducted in a motionless electrolyte at a temperature of 18°. The method of polarized measurements did not differ from the one described earlier [8].

Measurement Results

As in the experiments made by N.A. Izgaryshev, the polarization taking place when Cd was deposited from a pure sulfate solution was found to be negligible. Introducing a colloid into the electrolyte resulted merely in slightly diminishing the limiting diffusion current, due chiefly, it seems, to an increase in the viscosity of the electrolyte. Thus, the limiting current, with is 15 milliamp/cm^2 for a pure solution, dropped merely to 10-12 milliamp/cm^2 when 5 grams of gelatin per liter was added. The potential – current density curve represented the usual

case of concentration polarization with the onset of hydrogen discharge at high current densities.

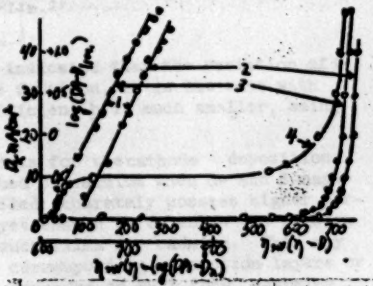
Introducing any one of our five additives (α- and β-naphthol, thymol, xylenol, and diphenylamine) into a similar electrolyte containing 1 gram of gelatin per liter did not result in any essential change in the shape of the curves. In view of the considerable increase in the efficiency of action of the surface-active substances when a colloid is added to tin electrolytes, we repeated these tests, but with the gelatin content increased to 5 grams per liter. In this case we were able to find a notable decrease in the limiting current when thymol and the α- and β-naphthols were added. The values of $D_{lim.}$ for this series of tests are given in Table 2.

TABLE 2

Limiting Currents (D in milliamp/cm^2) for Electrolytes Saturated with Additives

Composition of the solution: 0.25 N $CdSO_4$, 0.065 N H_2SO_4, 5 grams gelatin per liter. Temp.: 18°. Stationary Electrolyte

Test No.	Name of additive	$D_{lim.}$, mA/cm^2
1	Diphenylamine	9.0
2	Xylenol	9.0
3	α-Naphthol	6.8
4	β-Naphthol	6.4
5	Thymol	4.8
6	Gelatin alone	10.0



η/D curves and their analysis for the deposition of cadmium from a 0.25 N solution of $CdSO_4$ with additions of surface-active substances and gelatin.

The table shows that the effectiveness of the action of additives was still not high enough. In the best case all that we were able to achieve was cutting the limiting current in half. In our subsequent experiments we endeavored to reduce the limiting current still lower by introducing several surface-active substances into the electrolyte simultaneously. The first experiment, made with the solution simultaneously saturated with all five additives at once, yielded a very interesting result, namely: the limiting current dropped to 0.4 milliamp/cm^2 in this case, i.e., it was of the order of the lowest values of Dlim. for the deposition of tin.

The combined introduction of various additives also affected the appearance of the deposit – it changed from the matte finish produced when gelatin and any single one of the additives were added to a mirror-bright finish.

Subsequent experiments, in which we tried out the simultaneous action of two additives, showed that an exceptionally low limiting current is found to exist for a saturated solution of α-naphthol and diphenylamine. The numerical data for these experiments are listed in Table 3.

It is characteristic that the polarization occurring here not only much exceeds the η_{Sn}, but is the highest of all the known values of η for cathode deposition of the metals.

As the figure shows, the general shape of the curve resembles the corresponding functions for tin, differing from the latter solely in the smaller variation of the potential with the current in the third section of the curve. We were thus

able to state that the sharp braking of the electrode process exhibited in the deposition of Sn, due to the formation of a dense adsorption film of some surface-active substances, which is nearly impermeable for discharging ions, is likewise characteristic of cadmium deposition. In the light of this circumstance we endeavored to make a quantitative check of these experimental data. Unfortunately, the first section of the η/D curve is so tiny in this instance as to escape analysis, and this latter is complicated still further by the presence of appreciable chemical polarization when Cd is deposited from pure solutions. That is why we confined ourselves to checking the agreement of the experimental data for the third section of the curve with the approximate equation we had derived earlier, bearing in mind the logarithmic relationship between the polarization and the density of the current expended for the mechanism of discharge in the third section of the curve (i.e., subtracting $D_{lim.}$):

$$\eta = a - b \log (DA - D_{lim.}).$$

The results of these computations (see figure) indicated that the variation of η with log $(DA - D_{lim.})$ is nearly a straight-line function, as is the case with tin, differing from the latter in that the coefficient b is much smaller, being ~ 0.050 volt in this instance.

Comparison of experimental data with the data for the cathode deposition of tin indicates that the adsorption films formed on cadmium when α- and β-naphthols, thymol, xylenol, or diphenylamine are added separately possess higher permeability. Unfortunately, this data does not yet enable us to solve the problem of the reason for the lower braking action of such films for cadmium. This may be due either to the greater porousness of the corresponding adsorption layers or to their increased permeability for Cd^{++} ions, compared to Sn^{++} ions, assuming approximately identical structures in both cases. We shall return to this problem in one of our forthcoming papers.

In contrast to this, the combined addition of the additives results in marked retardation of the entire electrode process (low limiting current), which seems to indicate very low permeability of the adsorption films that are formed. In considering the foregoing data, we must bear in mind that the additives examined were extremely few in number. We must therefore expect that surface-active compounds may yet be found for cadmium plating that are even more efficient than those investigated.

It is worthy of note that the material role played by a colloid in the electrolyte, together with that of a capillary-active substance, as observed in the case of tin, is very striking in the case of cadmium. It is likewise characteristic that when diphenylamine, α-naphthol, and gelatin are all present in the electrolyte at the same time, reducing the concentration of gelatin from 5 grams per liter to 1 gram per liter sharply impairs the deposit and changes the nature of the electrode process very materially. Table 4 shows the variation of the potential with the current density for solutions containing α-naphthol, diphenylamine, and varying amounts of gelatin.

This indicates that the magnitude of the limiting current rises greatly as the gelatin concentration drops, while the polarization falls.

The sharp increase in the action of surface-active substances when gelatin is added is apparently due in part to the colloid's reinforcing the adsorption film. This effect is also, however, largely the result of the formation of ionic-colloidal adsorption coordination compounds (according to N.A.Izgaryshev [9]) in the solution and especially in the film at the electrode (high density of the colloid), which hamper the penetration of ions through the adsorption layer.

In conclusion, we should point out that, aside from some specific properties

Table 2

Potential as a Function of Current Density for the Deposition of Cadmium in the Presence of Surface-Active Substances and a Colloid

Composition of the solution: 0.25N $CdSO_4$; 0.05N H_2SO_4; and 5 g of gelatin per liter. Temperature: 18°. Stationary electrolyte.

Solution saturated with α- and β-naphthols, thymol, xylenol* and diphenylamine $D_{lim.}$ = 0.4 mA/cm²					Solution saturated with α-naphthol and diphenylamine $D_{lim.}$ = 0.36 mA/cm²					Without additives $D_{lim.}$ = 10 mA/cm²		
Test No.	D mA/cm²	-η mV	Current yield A%	log (DA - D_{lim})	Test No.	D mA/cm²	-η mV	Current yield A%	log (DA - D_{lim})	Test No.	D mA/cm²	-η mV
1	0.2	29.0	-	-	1	0.1	45.0	-	-	1	0.1	8.0
2	0.4	140.0	-	-	2	0.4	230.0	-	-	2	0.2	12.0
3	0.6	476.0	-	-	3	0.6	343.0	33.0	-	3	0.4	20.0
4	1.0	616.0	40.0	-	4	1.0	580.0	38.0	-	4	0.6	24.0
5	1.4	654.0	42.0	-0.72	5	1.4	618.0	42.0	-0.638	5	1.0	30.0
6	2.0	678.0	43.0	-0.34	6	2.0	645.0	48.0	-0.222	6	1.4	33.0
7	3.0	696.0	48.0	+0.16	7	3.0	663.0	53.0	+0.090	7	2.0	34.0
8	4.0	704.0	52.0	+0.32	8	4.0	673.0	58.0	+0.292	8	3.0	37.0
9	6.0	711.0	60.0	+0.58	9	8.0	684.0	62.0	+0.526	9	4.0	39.0
10	10.0	721.0	59.0	+0.77	10	10.0	691.0	63.0	+0.773	10	6.0	47.0
11	14.0	727.0	57.5	+0.91	11	14.0	700.0	65.0	+0.942	11	8.0	62.0
12	20.0	738.0	55.5	+1.05	12	20.0	711.0	67.0	+1.116	12	10.0	126.0
13	30.0	746.0	52.0	+1.19	13	30.0	723.0	70.0	+1.306	13	12.0	544.0
14	46.0	751.0	50.0	+1.30	14	46.0	735.0	71.0	+1.448	14	14.0	586.0
					15	50.0	748.0	65.0	+1.507	15	20.0	656.0
										16	30.0	698.0
										17	46.0	729.0
										18	50.0	730.0

*The solubility of the naphthols, xylenol and thymol is about 1 g per liter, and that of diphenylamine is 0.2 - 0.3 g per liter.

TABLE 4

Effect of a Colloid on Polarization in the Deposition of Cadmium From Solutions Containing Surface-Active Substances as Additives

Composition of the solution: 0.25 N Cd^{++} and 0.065 N H_2SO_4; solution saturated with diphenylamine and α-naphthol

Test No.	Dx, mA/cm²	Polarization, π, millivolts				
		Without gelatin	With gelatin			
			1 g/liter	2 g/liter	4 g/liter	5 g/liter
1	0.1	14.0	8.0	36.0	107.5	125.0
2	0.2	32.0	16.0	81.6	119.0	503.1
3	0.4	56.0	28.0	106.2	125.0	568.0
4	0.6	81.0	42.0	114.0	127.0	613.5
5	1.0	92.0	88.5	120.0	586.0	703.0
6	1.4	98.0	94.0	122.5	625.4	709.6
7	2.0	101.0	97.6	124.0	649.5	713.0
8	3.0	106.6	100.0	127.0	659.0	715.0
9	4.0	115.0	103.0	130.0	663.0	717.8
10	6.0	139.0	108.5	583.0	666.0	719.0
11	8.0	574.0	548.0	-	-	-
12	10.0	597.0	583.2	620.6	673.2	722.2
13	14.0	614.0	591.0	649.0	682.0	725.0
14	20.0	635.0	608.0	658.3	689.0	730.0
15	30.0	662.0	622.7	670.0	707.2	739.9
16	40.0	675.0	634.0	681.0	720.0	750.0
17	50.0	683.0	643.0	689.5	728.8	758.0
18	60.0	691.0	-	696.0	738.0	-

of the cathode deposition of cadmium in the presence of the capillary-active additives referred to, the variation of the potential with the current density for cadmium is of the same type as in the case of tin, which points to a similar mechanism operating in both cases.

The higher values for polarization as compared with the discharge of tin from solutions containing the same additives are in good agreement with the greater difference between the process' equilibrium potential and the surface's zero-charge point in this instance ($\Delta\varphi_{Cd} = 0.4$; $\Delta\varphi_{Sn} = 0.2$ volts), which causes the adsorption film to begin breaking down at higher values of η.

SUMMARY

1. A study has been made of cathode polarization in the deposition of cadmium from pure solutions of $CdSO_4$ and from solutions containing phenols, diphenylamine, and gelatin as additives.

2. It has been found that the discharge of cadmium ions from solutions that are saturated with diphenylamine and α-naphthol and contain a colloid is accompanied by very high chemical polarization, which far exceeds the overvoltage occurring during the deposition of metals of the iron group.

3. The variation of the potential with the current density that exists in this case is similar to the shape of the polarization curves for the deposition of tin in the presence of various organic surface-active substances in the electrolyte and is in good agreement with the hypothesis that dense adsorption films are formed on the electrode and that they are broken down (desorption) when the negative potentials on the electrode are high enough.

4. The increase in the effectiveness of the additives produced by the addition of gelatin is the result of the formation of Izgaryshev adsorption ionic-colloidal coordination compounds in the solution and in the film surrounding the electrode, which hamper the penetration of the ions through the adsorption layer.

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THE DEPENDENCE OF SOME REDOX REACTIONS UPON THE pH OF THE MEDIUM

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Numerous comprehensive scientific papers have been written on the effect of H^+ ions upon oxidative-reducing reactions, and still this problem has not been resolved satisfactorily for inorganic reactions, [1]. We might state at this point, by the way, that the overwhelming majority of these papers deal only with individual reactions or groups of reactions, and the accumulation of a vast amount of experimental data has not resulted in any notable generalizations in the field of inorganic chemistry as yet.

In selecting the optimum medium (i.e., the numerical pH value) for oxidative-reducing (redox) reactions, the sole guiding principle employed up to the present time is founded upon balancing the H^+ ions in the equations for these reactions. This principle, initially proposed by Mohr [2] is phrased about as follows at the present time: If the concentration of H^+ ions in the solution rises as the result of a given reaction, the reaction is promoted by an alkaline medium, while an acid medium will be best if the concentration of OH^- ions rises.

Representing a special case of the Law of Mass Action, this principle is borne out by the experimental results in most cases, but it possesses the two following deficiencies. First, determination of the optimum medium always requires the setting down of the equations for the chemical reactions involved, in such a way as to enable the correct drawing up of the hydrogen-ion balance-sheet. This condition sometimes entails very complicated computations and therefore is not complied with in such cases, as will be shown later on. Second, even with the most precise balance-sheet of the H^+ ions in the equations for the chemical reactions, this principle often contradicts reality and hence is not free of inherent flaws.

In 1900, F. Crotogino [3] proposed, on the basis of considerable experimental data, that all special redox systems be divided into two classes. His first class comprised the systems whose oxidized forms contained oxygen, such as:

$$MnO_4^- + 5e + 8H^+ \rightleftarrows Mn^{2+} + 4H_2O;$$

$$ClO_3^- + 6e + 6H^+ \rightleftarrows Cl^- + 3H_2O;$$

the second class comprising all the others, such as:

$$Fe^{3+} + e \rightleftarrows Fe^{2+}; \qquad I_2 + 2e \rightleftarrows 2I^- .$$

At the same time, the author demonstrated that the numerical values of the oxidation potentials of Class I systems are increasing functions of the hydrogen-ion concentration, while the values of the potentials of Class II systems are

independent of the medium, provided, of course, the changes in the pH do not involve any side processes in these systems.

This paper was also the first to propose the well-known equation stating the variation of the oxidation potentials of Class I systems with the hydrogen-ion concentration in the solution, the chemical reaction occurring in the system and this equation being expressed as follows in the original paper:

$$nOx + mH^+ \rightleftarrows n'Red + mOH^- + sF \qquad (1)$$

$$E = \frac{RT}{sF} \ln K \frac{O_x^n [H^+]^{2m}}{Red^{n'} K_w^m}, \qquad (2)$$

where K is the constant characterizing the given system and K_w is the ionization constant for water. (As we know, these equations are written differently nowadays, but their content has remained the same.).

This classification of singular redox systems with respect to the large group of universal redox systems makes it unnecessary to draw up a hydrogen-ion balance sheet for chemical equations; this eliminates in part one of the above-mentioned deficiencies of Mohr's principle. The value of this classification becomes obvious if we follow the example of A.K.Babko [4] and divide all redox reactions into four groups, depending on the classes of special redox systems taking part in these reactions.

Yet it may be shown that any conclusions drawn from Crotogino's classification and equations concerning the optimum medium for redox reactions always coincide with the conclusions based upon the hydrogen-ion balance, although these conclusions are contradicted by reality in some instances. Thus, the cited paper by Crotogino, while facilitating the use of an effective principle for determining the optimum medium for redox reactions, does not eliminate the inherent flaw in this principle.

The inadequacy of the theory under discussion is exhibited principally in the redox reactions in which both the oxidizing and reducing special systems belong to Crotogino's Class I. The reason for this is the fact that, according to present theory, the part played by the hydrogen and hydroxyl ions in these reactions consists solely in their mutual neutralization.

In much better agreement with all the major experimental data is the assumption that the hydrogen ions perform another and no less important function, besides their neutralizing the OH^- or O^{2-} ions, namely: they break down complex anions of the EO_x^{I-} type (such as MnO_4^-) in such a way as to evolve oxygen as one of the end products [5]. The well-known fact that the degree of stability of anions of the EO_x^{I-} type against the action of protons also depends upon the nature of these anions, and not merely upon the H^+ or OH^- ion balance in the equations for these reactions, fully conforms to this assumption. There is no doubt that a disturbance of the stability of the EO_x^{I-} anion increases its oxidizing power [6].

The auxiliary function of the hydrogen ions mentioned above, though exerting a material effect upon redox processes, is not reflected in Equation (2), nor is it accounted for by any other hypotheses.

We selected the following three reactions: the oxidation of an arsenite by a bromate and a chlorate and the oxidation of a sulfite by a chlorate, for research as examples of such redox systems, in which the oxidative and reducing special systems both belonged to Crotogino's Class I.

According to the currently accepted theory, all these reactions (and those similar to them) require an alkaline or neutral medium, whereas the new concept set forth above states that only raising the acidity of the medium will promote these reactions, despite the fact that each of these reactions doubtless results in raising the hydrogen-ion concentration in the solution to some extent. It is the object of the present paper to provide an experimental check of this new concept of the effect of the medium's pH on redox reactions in the foregoing reactions. In our discussion of each of the reactions we shall also compare the existing and the proposed theories.

I. Oxidation of An Arsenite by A Bromate

This reaction has been employed for a long time [7,8] in bromatometry and is therefore of great interest, theoretically as well as practically. According to current theory, selecting the optimum pH value of the solution for the reaction in question requires the preliminary determination of the hydrogen-ion (or hydroxyl-ion) balance-sheet in the chemical equation, but this determination is not feasible if there are no figures on the numerical pH value, inasmuch as this balance sheet depends upon the pH level. The experimental data indicate that the reaction in question is satisfactory only when the acidity of the solution is at least 1N.

Under these conditions setting up the chemical equation that would enable us to compute the hydrogen-ion balance-sheet for the reaction becomes very difficult, since the reduced arsenic appears in various forms (such as As^{3+}, H_3AsO_3, $As(OH)_2^+$, etc.) in this reaction, and it proves to be rather hard to compute the proportions in which they are present, while the predominance of one form or another of the arsenic affects the hydrogen-ion balance in the reaction.

Kolthoff and Sendell [9], for instance, give the following equation for this reaction:

$$3As^{3+} + BrO_3^- + 6H^+ = 3As^{5+} + Br^- + 3H_2O. \qquad (3)$$

Though this equation is in harmony with the classical principle of selecting the optimum medium for redox reactions, it is actually an artificial one beyond a doubt, contradicting reality, inasmuch as there is absolutely no reason for expressing As^V by the As^{5+} ion. When the medium is highly acid there are much more data to support the assumption that arsenic acid is the dominant form of the arsenate. But then the reaction equation will be just the opposite as far as the hydrogen-ion balance is concerned (retaining the previous form of the reduced arsenic):

$$3As^{3+} + BrO_3^- + 9H_2O = 3H_3AsO_4 + Br^- + 9H^+. \qquad (4)$$

Nor does this equation satisfactorily reflect the true nature of the process, however, inasmuch as the As^{3+} ion is also not the predominant form of the reduced arsenic.

Without going into further details of the hydrogen-ion balance-sheet, we may state categorically that performing the foregoing reaction in an acid medium results in increasing the concentration of hydrogen ions in solution, even though the reaction is assisted by an acid medium.

According to our new point of view, the problem of the optimum medium for this reaction is resolved in practice wholly independently of the hydrogen-ion balance. We know that an arsenate resists the action of protons better than a bromate does and that, in any event, they do not cause it to oxidize oxygen anions. In an alkaline or neutral medium a bromate is a very weak oxidizing agent, while its oxidative properties increase so much when the medium is sufficiently acid that the reduction of bromine is accompanied by the evolution of free oxygen, unless the reaction medium contains a suitable reducing agent. Hence, increasing

the acidity of the medium will promote the reaction under discussion.

Research Method

Equal volumes of the following solutions: potassium arsenite neutralized with hydrochloric acid against methyl orange, potassium bromate, and hydrochloric acid, were mixed together in a bottle with a ground-glass stopper. In all our tests the concentrations of the arsenite and the bromate in the mixture were about 0.1 N, the concentration of the hydrochloric acid being varied from test to test. The original solutions were kept in a water thermostat at 15°, and the reaction mixture was placed in the same thermostat. At given intervals of time batches of the reaction mixture (usually 10 ml each) were removed, and the residue of arsenite measured iodometrically after they had been neutralized with sodium bicarbonate.

Research Results

If the pH $\geq$ 4, the arsenite is not oxidized even afer a month has passed (at room temperature). As is seen in Fig. 1, the velocity of this reaction becomes practically perceptible when the HCl concentration reaches 0.05 N.

The shape of the curves in Fig. 1, particularly Curve 2, points to the autocatalytic nature of the process in question.

During the initial intervals of time, which are different for different pH values, the reaction velocity is negligible, but then it rises, falling again later on.

We had to find out which of the reaction products acted as a catalyst. When the acidity of the solution is 0.1N (Curve 2), the As^{III} and the As^{V} will evidently be present as the respective acids, and then the reaction may be expressed by means of this equation:

$$3H_3AsO_3 + BrO_3^- = 3H_3AsO_4 + Br^-. \quad (5)$$

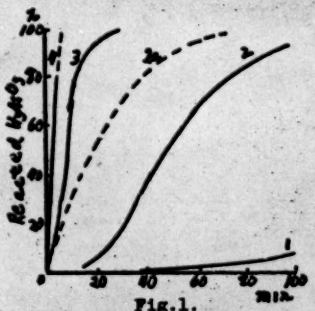

Fig. 1. Kinetics of the oxidation of an arsenite by a bromate. The HCl concentrations were 0.05N, 0.1N, 0.2N, and 0.3N for Curves 1, 2 (2a), 3, and 4, respectively.

Besides the arsenate and the bromide, H^+ ions also accumulate in the solution as a reaction product, inasmuch as arsenic acid is stronger than arsenious acid, but when the acidity of the solution is no lower than 0.1N, the electrolytic dissociation of the H_3AsO_4 is so depressed that the increase in the concentration of H^+ ions may be neglected. We therefore had to test the influence of only the bromide and the arsenate, knowing as we did concerning the former [10] that it accelerates the given reaction, but we tested this phenomenon under our experimental conditions. Our investigations showed that when 0.01 mg of KBr was added per milliliter, the course of the reaction was changed materially, as indicated by Curve 2a: both the induction period and the positive acceleration of the reaction, which are present when no foreign bromide is added, disappear. The arsenate has no effect upon the course of the reaction. Thus, there is no doubt that the autocatalytic action in this reaction is due to the bromide.

The manner in which the bromide affects the velocity of the reaction in question may evidently be understood in the light of the following facts. At a pH = 1, Reaction 5 takes place slowly, while the reaction velocities of

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O \quad (6), \qquad \text{and}$$

$$H_3AsO_3 + Br_2 + H_2O = H_3AsO_4 + 2Br^- + 2H^+ \quad (7)$$

are several hundred per cent higher. Hence, Equation (5) must be looked upon chiefly as an overall expression for two consecutive reactions, (6) and (7).

The variation of the reaction velocity with the pH is similar in a sulfuric acid medium, but the reaction is slower than in a hydrochloric-acid medium for equal activity of the H^+ ions.

II. Oxidation of an Arsenite by a Chlorate

All the theoretical conditions reported for the foregoing reaction are wholly applicable to the present case. We must merely bear in mind that a chlorate resists the action of H^+ ions better than does a bromate, which is evidently why the present reaction requires a still more acid medium.

The research method used was the same as in the previous instance. A guaranteed preparation of Berthollet's salt served as our chlorate. The test results indicate that at a pH $\geqslant 4$ (room temperature) the reaction in question does not take place within one month. Data in Fig. 2 indicate that the reaction velocity becomes perceptible only when the HCl concentration rises to 2N. Any further increase in acidity raises the reaction velocity markedly. No autocatalysis is observable in this case. Thus, this reaction requires higher acidity of the medium than did the previous reaction.

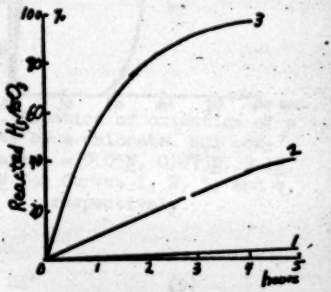

Fig. 2. Kinetics of oxidation of an arsenite by a chlorate. HCl concentrations 2N, 3N, and 4N, for Curves 1, 2, and 3, respectively.

III. Oxidation of a Sulfite by a Chlorate

The oxidized form of the reducing system in this reaction is S^{VI}. As we know, this form acts as an oxidant only when it is present as concentrated sulfuric acid, while the chlorate behaves like the bromate. These facts indicate that a rise in the acidity of the medium will promote this reaction.

Research Method

We know that a sulfite is rapidly oxidized by atmospheric oxygen when in an aqueous solution. Hence the solutions of all the reagents were prepared with boiled distilled water, while any air subsequently entering the flask containing the water first passed through an alkaline solution of pyrogallol. The prepared solutions were kept in small, hermetically sealed flasks; the solution in any one flask was used for only one test. But even these precautions were unable to prevent the above-mentioned side reaction entirely, so that we had to judge the velocity of the reaction involving the oxidation of the sulfite by the chlorate chiefly by the change in the concentration of the chlorate rather than that of the sulfite. The concentration of the sodium sulfite was 0.11-0.12N, that of the potassium chlorate 0.1 N, and that of the hydrochloric acid varied from zero to 1N. The vessel containing the reaction mixture was kept in a thermostat at 15° together with the vessels containing the original solutions. At fixed intervals of time aliquot parts of the reaction mixture (10 ml each) were neutralized with sodium bicarbonate, then an excess of 0.1N iodine solution was added, and the residue of the latter titrated back with a 0.1N solution of thiosulfate; then the sulfite that had not reacted with the chlorate was similarly determined. The results of this determination served as an index to the progress of the reaction.

The residual chlorate in the back-titrated samples was determined according to Kolthoff's method [8], after it had been established that the tetrathionate formed in the reaction mixture as a product of the previous determination did not affect the determination of the chlorate.

Research results. When no acid was present, no oxidation of the sulfite by the chlorate was observed during the course of one month. Nor was this reaction found to occur during 7 hours in a 0.025N solution of hydrochloric acid. In 0.05N

HCl there is a certain induction period, during which the reaction velocity is negligibly small and hence hard to observe; then, after 20 to 40 minutes, the reaction begins to gain speed, and finally the reaction rate drops again. The induction period grows with the concentration of sulfite (for a constant concentration of HCl, 0.05N).

The curves representing the velocities of the reactions that have an induction period are similar on the whole; one of these curves is shown in Fig. 3 (Curve 1). The numerical value of the pH of the solution that contained 0.05N HCl and 0.1N Na_2SO_3 was approximately 4.3. We were interested in the circumstance that no oxidation of the chlorate occurred after a whole day in a buffer solution with the same pH value (a 0.5N solution of NaH_2PO_4).

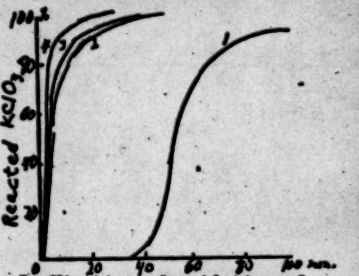

Fig.3. Kinetics of oxidation of a sulfite by a chlorate. HCl concentration = 0.05N, 0.075N, 0.1N, and 1N for Curves 1, 2, 3, and 4, respectively.

The nature of the velocity of this process and, in particular, the presence of an induction period may be explained as follows. In the initial state of the system, the numerical value of the pH does not ensure this process rate, as might have been easily observed, but the reaction proceeds nonetheless, H^+ ions accumulating as one of its products:

$$ClO_3^- + 3HSO_3^- = Cl^- + 3SO_4^{2-} + 3H^+. \qquad (8)$$

It is not impossible that a side reaction takes place involving atmospheric oxygen at any pH value, which likewise results in increasing the acidity of the medium:

$$O_2 + 2HSO_3^- = 2SO_4^{2-} + 2H^+ \qquad (9)$$

The reaction velocity rises as the H^+ ions accumulate. But, according to the Law of Mass Action, acceleration of the reaction must change in sign at a certain instant, i.e., its velocity passes through a maximum.

In 0.075n HCl the reaction takes place without any induction period (Fig. 3, Curve 2). Any further increase in the acidity of the solution merely increases the velocity of the given reaction slightly (Fig. 3, Curves 3 and 4). Hence, the oxidation of a sulfite by a chlorate is also promoted by an increase in the acidity of the solution, the velocity of this reaction rising suddenly when the HCl concentration rises to 0.05N (with a 0.1N solution of Na_2SO_3).

SUMMARY

1. A study has been made of the effect of the hydrogen-ion concentration upon the reaction velocity of the oxidation of an arsenite by a bromate and a chlorate and of a sulfite by a chlorate.

2. It has been found that a prognosis regarding the variation of the velocity of these reactions with the pH of the medium that is based upon the Law of Mass Action alone is not borne out by experiment.

3. It has been shown that this variation of the reactions with the pH may be forecast correctly by making allowance for the catalytic action of the H^+ ions, which causes deformation of the bromate and chlorate anions.

4. It has been found that these reactions practically do not take place at all unless the hydrogen-ion concentration of the reaction medium reaches a certain level, which differs for each reaction. A further rise in the acidity causes a sharp increase in the reaction rate.

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RESEARCHES ON SYSTEMS CONTAINING FORMIC ACID V.

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This paper presents the results of an investigation of the formic acid – nicotine, formic acid – piperidine, and formic acid – anabasine systems by the viscosity and density methods.

We used formic acid with a melting point of 8.3°, nicotine with a boiling point of 111-112° at 6 mm, piperidine with a boiling point of 103.8° at 720 mm, and anabasine with a boiling point of 140-141° at 10 mm in this research.

Formic Acid – Nicotine System

The results of the viscosity and density measurements at 25, 50, and 75°C are given in Table 1. All the viscosity isotherms pass through a sharply marked maximum. On the 25° viscosity isotherm the maximum lies at 34 mol.% of nicotine, while it is situated at 31 mol.% on the 75° isotherm. Thus, in this system the viscosity is shifted toward the less viscous constituent: formic acid. Very intense heating was observed when the mixtures were made, especially when the proportions corresponded to those for the maximum on the viscosity diagram, (Fig. 1).

Formic Acid – Piperidine System

The results of the viscosity and density measurements at 25, 50, and 75°C are given in Table 2. The viscosity isotherms shown in Fig. 2 pass through a marked maximum, located at 52 mol.% of piperidine. As the temperature is raised, the maximum on the viscosity isotherms hardly shifts at all along the axis of abscissas. Intense heating was observed when the constituents were mixed, which is why the original substances were first chilled before mixing. Mixtures whose compositions agreed with those of the maxima in the viscosity graph crystallized at temperatures that were below 10°.

Formic Acid – Anabasine System

The results of the viscosity and density measurements at 25, 50, and 75°C are given in Table 3. The viscosity isotherms are shown in Fig. 3, where only the 75° isotherm is shown in full. The viscosity curve for 75° has a singular point at 50 mol.%. We were unable to measure the viscosity of the equimolecular mixture at 50° or 25°, as the viscosity of the mixture was extraordinarily high. The constituents were chilled before the mixtures were made in order to prevent excessive heating, which would cause the solution to turn dark.

The sharp maximum on the viscosity isotherm of the formic acid – nicotine

TABLE 1.

Formic Acid – Nicotine

Mol.% of nicotine	Viscosity			Density		
	25°	50°	75°	25°	50°	75°
0.00	1.5428	0.9815	0.6825	1.1998	1.1796	1.1564
7.22	10.4794	5.1128	2.8991	1.2167	1.1948	1.1682
10.07	15.9257	6.9110	3.6286	1.2185	1.1968	1.1709
11.58	18.9870	7.5485	4.1171	1.2170	1.1961	1.1678
20.33	45.6783	15.8351	7.0858	1.1884	1.1676	1.1475
24.93	69.1276	10.2927	8.0566	1.1784	1.1524	1.1332
26.37	77.7541	21.0044	8.4393	1.1769	1.1528	1.1329
26.56	81.2538	21.3557	8.5468	1.1716	1.1489	1.1298
30.36	107.8897	26.8927	10.0551	1.1607	1.1404	1.1200
30.38	109.8629	27.2498	10.3189	1.1589	1.1394	1.1189
30.95	112.2486	27.3560	10.3365	1.1578	1.1379	1.1175
31.86	115.6579	27.5275	10.2474	1.1571	1.1369	1.1157
32.94	116.1270	26.8571	9.7926	1.1529	1.1321	1.1115
33.33	117.9098	25.9154	9.7017	1.1515	1.1309	1.1113
34.26	119.1699	26.2720	8.7529	1.1507	1.1260	1.1056
34.42	117.3447	26.2196	9.7604	1.1484	1.1254	1.1048
35.35	114.8170	25.5798	9.4709	1.1480	1.1234	1.1028
36.62	109.4042	24.2307	9.0319	1.1432	1.1199	1.1004
39.92	92.1480	20.8496	7.7813	1.1319	1.1110	1.0886
50.03	37.6467	11.4266	4.7785	1.0953	1.0733	1.0524
58.31	20.5651	7.6102	3.3052	1.0704	1.0466	1.0232
71.44	10.1264	3.9645	2.1200	1.0460	1.0234	0.9995
79.56	6.4266	2.9629	1.6586	1.0273	1.0077	0.9835
88.60	4.6957	2.4213	1.4534	1.0146	0.9969	0.9742
100.00	3.8942	2.0376	1.2626	1.0068	0.9866	0.9670

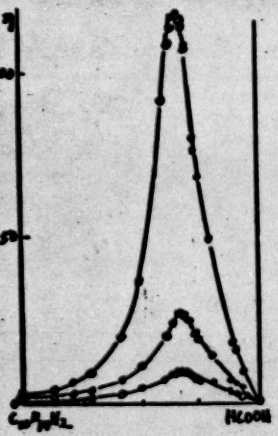

Fig. 1.

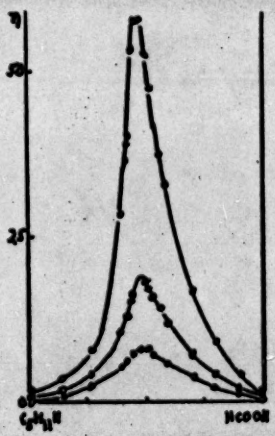

Fig. 2.

TABLE 2

Formic Acid – Piperidine

Mol. % of piperidine	Viscosity			Density		
	25°	50°	75°	25°	50°	75°
0.00	1.5428	0.9815	0.6825	1.1998	1.1796	1.1564
10.31	4.1395	2.2673	1.4493	1.1664	1.1504	1.1285
20.07	9.0016	4.4002	2.6019	1.1389	1.1200	1.1010
30.75	16.8070	7.3325	3.8769	1.1066	1.0873	1.0673
41.04	32.7308	12.2166	6.2167	1.0774	1.0590	1.0419
44.11	38.0514	14.4649	6.6915	1.0674	1.0506	1.0304
47.66	48.0201	17.1799	7.4748	1.0609	1.0438	1.0239
50.33	52.6698	18.2871	7.1080	1.0571	1.0340	1.0147
52.35	57.5083	19.2808	8.3795	1.0497	1.0254	1.0066
54.79	52.5687	17.2106	7.2316	1.0405	1.0216	1.0004
56.00	40.0852	15.2806	6.8506	1.0340	1.0109	0.9908
56.43	39.3624	14.6843	6.6682	1.0304	1.0101	0.9900
58.52	34.9870	12.3993	6.2096	1.0233	1.0039	0.9828
60.57	27.9437	10.5611	5.0027	1.0116	0.9915	0.9738
73.19	8.7065	4.0507	2.2339	0.9525	0.9329	0.9111
85.76	3.1215	1.6803	1.0107	0.9054	0.8782	0.8562
100.00	1.3372	0.8403	0.5596	0.8567	0.8313	0.8063

TABLE 3

Formic Acid – Anabasine

Mol.% of anabasine	Viscosity			Density		
	25°	50°	75°	25°	50°	75°
0.00	1.5428	0.9815	0.6825	1.1998	1.1796	1.1564
19.53	98.3189	27.0368	10.1411	1.2049	1.1844	1.1605
32.16	657.1579	140.6465	32.0243	1.1695	1.1571	1.1386
49.81	–	–	190.2348	–	–	1.1000
62.36	4112.6965	2424.2071	38.9524	1.1139	1.0970	1.0720
76.91	336.3152	44.3587	11.7879	1.0768	1.0626	1.0426
100.00	25.1976	7.1385	3.1541	1.0427	1.0237	1.0003

system (Fig. 1) located at approximately 33 mol.% of nicotine, testifies to the formation of a chemical compound. This is also indicated by the large amount of heat liberated when the constituents are mixed. In this system the constituents react together in the liquid phase to form a compound with the formula $2HCOOH \cdot C_{10}H_{14}N_2$. The formic acid – nicotine system is like the chloral – water system [1]. As in the chloral – water system, the maxima on the viscosity isotherms are slightly shifted toward the less viscous constituent as the temperature is raised. This shift of the maximum along the axis of abscissas toward the formic acid may be due to the fact that the compound that is formed is partially dissociated into its constituents as the temperature rises, or by the fact that nicotine has a higher

Figure. 3.

temperature coefficient of viscosity than formic acid. Yet we know that in some cases the viscosity maximum may also be shifted when the compound that is formed reacts with one of the constituents [2]. This shift of the maximum may take place either as the result of the action of one of these factors or because of any combination of them; the latter apparently was true in our instance.

The shape of the viscosity isotherms of the formic acid – piperidine system resembles those in the formic acid – pyridine system [3]. As in the formic acid – pyridine system, the sharply marked maxima on the viscosity isotherms of the formic acid – piperidine system are shifted somewhat from the rational proportion of the components and exhibit practically no shift with a change in temperature. The compound that is formed with the evolution of considerable heat is completely stable and can be crystallized at a temperature below 10°. An equimolecular compound is formed in the formic acid – anabasine system, as is indicated by the singular point on the 75° viscosity isotherm (Fig. 3). A thick, extremely viscous mass results when the constituents are mixed together. As the temperature is lowered, the equimolecular mixture of the components of this system grows turbid and is transformed into a hyaline mass, but does not crystallize. Apparently, we did not employ suitable conditions. If the correct conditions are found, we ought to be able to produce the equimolecular compound of this system in crystalline form. It is worthy of note that anabasine adds one molecule of acid when two basic nitrogen atoms are present, whereas nicotine adds two molecules of the acid when two basic nitrogens are present.

SUMMARY

1. A study has been made of the formic acid – nicotine, formic acid – piperidine, and formic acid – anabasine systems by the viscosity and density methods at 25, 50, and 75°C.

2. It has been found that formic acid forms a compound with the formula $2HCOOH \cdot C_{10}H_{14}N_2$ with nicotine, with the formula $HCOOH \cdot C_5H_{11}N$ with piperidine, and with the formula $HCOOH \cdot C_{10}H_{14}N_2$ with anabasine.

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THE PHYSICO-CHEMICAL ANALYSIS OF TERNARY AQUEOUS SYSTEMS CONSISTING OF FLUORIDES OF THE ALKALI-EARTH METALS AND FLUORIDES OF THE ALKALI METALS

I. THE TERNARY SYSTEMS BaF_2-KF-H_2O AND BaF_2-NaF-H_2O AT 25°

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The elaboration of new fluorometric methods in analytical chemistry demands the fullest and manysided study of various properties of the simple and complex fluorides, mainly their solubilities, their stability, and the conditions governing their formation in aqueous solutions. This study can be best accomplished by the methods of physico-chemical analysis of the aqueous systems comprising the fluorides and other electrolytes.

We have made a systematic study of ternary aqueous systems with fluorides of the alkali-earth metals.

This report presents the results of our research on the systems BaF_2 – KF – – H_2O and BaF_2 – NaF – H_2O at 25°.

We have been unable to find a single paper in the literature on ternary aqueous systems with barium fluoride and an alkali metal or ammonia.

The anhydrous system BaF_2 – KF has been investigated by means of the fusibility method by Bonashek and Bergman in 1947 [1]. Grube [2] investigated the BaF_2 – NaF system in 1927, likewise by means of the fusibility method. Both of these are simple eutectic systems. Grube's results have recently been corroborated by Benashek and Bergman [3]. But the absence of the formation of double salts in anhydrous systems at high temperatures by no means implies that they cannot be formed in aqueous systems at low temperatures. Nor have we any data on the solubility of BaF_2 in KF or NaF solutions. The figures in the literature on the solubility of BaF_2 in pure water given by various authors differ fairly appreciably.

EXPERIMENTAL

Constituents. The barium fluoride was prepared from Kalhbaum barium carbonate and 40% hydrofluoric acid, twice redistilled in a platinum still.* The resulting moist BaF_2, which contained an excess of HF, was dried out over a water bath and then slightly calcined until all the adsorbed HF had been driven off. Analysis of the finished preparation indicated that it contained 99.98% BaF_2.

*The hydrofluoric acid was purified in the analytical chemistry laboratory of the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences.

The potassium and sodium fluorides were prepared by accurately neutralizing dilute HF with caustic potash and caustic soda, respectively, against phenolphthalein. (Both of these alkalies were of Kalhbaum manufacture.) The KF and NaF solutions produced by neutralization served as the initial solutions for the preparation of solutions of the requisite concentration by evaporation or dilution. All the solutions were made up with double-distilled water (from a still fitted with a tin condenser).

Operational method. We investigated the equilibrium of the $BaF_2 - KF - H_2O$ and $BaF_2 - NaF - H_2O$ systems at 25° by the usual solubility method, consisting of keeping a series of mixtures of the constituents in various proportions for a rather long time in a thermostat, after which the saturated solution and the solid phase, impregnated with the mother liquor, were analyzed. The composition of the anhydrous solid phase was determined from these data by means of the Schreinemakers method.

The solutions were saturated in a special device, illustrated schematically in Fig. 1. The initial mixture of components was placed in the flask of the device, with a capacity of some 300 ml, and well stirred with a spiral stirrer, set in rapid motion by a motor. The other parts of the device shown in the diagram served in taking samples of the solution and the moist precipitate.

When suction was applied to the tube projecting upward from the glass hood, the saturated solution together with solid-phase particles suspended in it rose through the siphon tube into the hood, where it dropped into a small funnel containing a dry filter. The filtered solution was collected in the receiving flask, with a capacity of some 250 ml, attached to the hood by a rubber stopper.

The funnel may easily be withdrawn from the neck of the receiving flask and reinserted therein without disassembling the device, by means of the long wire attached to it, which passes through the tube projecting upward from the hood.

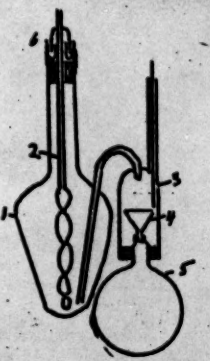

Fig. 1. Device for determining solubility.

1-Flask for the solution to be saturated; 2-stirrer; 3-hood; 4-funnel; 5-receiving flask for the filtered solution; 6-mercury seal.

The device enabled us to take samples of saturated solutions completely freed of solid-phase particles, with the temperature kept rigidly constant throughout the operation. At the same time as the samples of the solution were being taken, a sufficient quantity of the moist precipitate was collected on the filter, part of it being used for analysis after the device was disassembled. Because it was so easy to shift the funnel without having to dismantle the device, we could always discard the first runnings of the filtrate, letting them collect inside the hood between the hood walls and the neck of the receiving flask.

To protect the glass against the corrosive action of the fluorides, all parts of the device, with the exception of the hood, were coated on the inside with a layer of paraffin. All the flasks and bottles used for keeping the initial solutions and the samples taken were likewise paraffined.

After the device had been filled and assembled, it was placed in a water thermostat so that the water level in the thermostat was higher than the hood or the upper edge of the siphon tube. The temperature of the thermostat was kept at 25° ± 0.1° by means of a toluene thermoregulator.

When the receiving flask had been filled with the filtered saturated solution, the device was disassembled, and some of the solution was taken for determination of its specific gravity at 25°. The rest of the solution was transferred to a paraffined flask, weighed, and reserved for analysis. Samples of the moist precipitate were taken with a small celluloid spatula from the deposit on the filter paper immediately after the funnel was removed from the device, transferred to a covered platinum crucible, weighed, and then analyzed to determine all its constituents.

The procedure used in making up the initial mixtures of the constituents was as follows in most cases.

A solution of an alkali fluoride, whose titer was known accurately, was added from a gravimetric buret to a fixed weight of saturated BaF_2 solution in water. The ratio of the weights of the solutions to be mixed together was so chosen as to produce a solution of the desired concentration of alkali fluoride. When the solutions were mixed together, a precipitate invariably settled out as a fairly stable suspension. I. Tananaev and E.Deichman [4] have pointed out the advantages of such a procedure for mixing the constituents, which transforms the system from a supersaturated state into an equilibrium state.

In some of our tests we employed the opposite sequence of saturation steps, in which the system attained equilibrium from the unsaturated state. This was done by adding a small quantity of solid BaF_2 to a solution of the alkali fluoride whose concentration was known, after which the mixture was placed in a thermostat and subjected to constant vigorous stirring. The agreement of the results obtained by both procedures was further confirmation that the system had reached true equilibrium.

Investigation of the two systems was begun with the solutions with the highest concentrations of the alkali fluoride, inasmuch as it was under these conditions that any formation of new solid phases, distinct from BaF_2 and MeF, would be detected most readily. In view of the slowness with which equilibrium was established when we passed from one solid phase to another, we set the time that the mixtures were kept as two months* in the experiments in which they consisted of a solution of the alkali fluoride and solid BaF_2. When the mixture was made up of a saturated solution of BaF_2 in water and a solution of the alkali fluoride, we were working with a freshly precipitated solid phase that was stable under the given conditions, and in this case the mixtures were kept in a thermostat for 1 to 2 days.

In determining the solubility of BaF_2 in low-concentration solutions of the alkali fluoride, the required minimum thermostat time was established by means of special tests, which showed that the BaF_2 concentration in the solution becomes practically constant within 8-10 hours, no matter what method is used in mixing the constituents. For this reason we kept the mixtures in the thermostat for 10-12 hours in our experiments to measure the solubility of BaF_2.

The samples of the saturated solutions and the moist precipitates were analyzed to determine their BaF_2 and MeF content by converting the fluorides into sulfates, determining the aggregate weight of the sulfates, and then determining the weight of the $BaSO_4$ separately.

In every case the barium sulfate was freed of the coprecipitated sulfate of the alkali metal by the procedure laid down in the Hillebrand and Lendell manual [5]. The percentage of water in the moist precipitates was determined by desiccating the samples at 150° for the systems containing sodium fluoride

*The prepared mixtures of KF or NaF solutions and solid BaF_2 were saturated for most of this time in paraffin-coated bottles, in which they were continuously stirred by a motor, and then they were transferred to the device used to determine their solubility.

and by computation for the systems containing potassium fluoride – as the difference between the weight of the moist precipitate and the amount of barium and potassium fluorides it was found to contain upon analysis.

A check of the procedure we adopted for analyzing solutions consisting of synthetic mixtures indicated that the percentage error in our determinations of the amount of BaF_2 in the solutions ranged from 0.2% to 2% at concentrations of the alkali fluoride that did not exceed 0.05 mol per liter.

The percentage error rose as high as 8% for the highest concentrations of the MeF at which the solubility of BaF_2 was determined.

Experimental Results and Their Evaluation

The BaF_2 – KF – H_2O System

The composition of the solutions and the respective moist precipitates, expressed in per cent by weight, are shown graphically in the triangular diagram of Fig. 2.

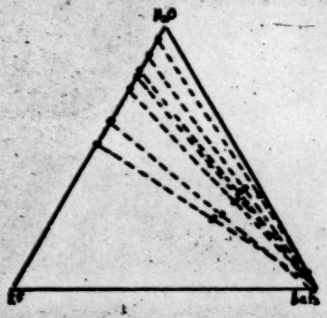

Fig. 2. Composition of the solutions and the moist precipitates in the BaF_2 – KF – H_2O system (% by weight).

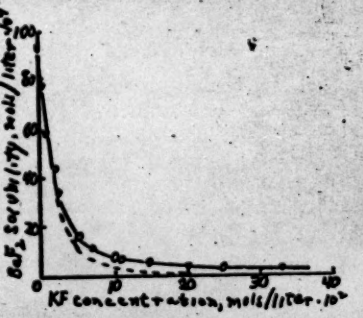

Fig. 3. Solubility of BaF_2 in the BaF_2 – KF – H_2O system.

As is seen from inspection of the diagram, all the nodes practically converge at the vertex of the triangle representing 100% BaF_2, even for the highest concentrations of the potassium fluoride in the solution.

Thus, it must be admitted that no double salts or solid solutions occur in this system at 25°. The values of the solubility of barium fluoride in a solution containing various concentrations of potassium fluoride obtained by us are listed in Table 1.

Our value for the solubility of barium fluoride in pure water is close to the value obtained by Kohlrausch by the electrical conductance method and is much higher than the value found by Carter.

According to Kohlrausch [6], the solubility of BaF_2 is $9.20 \cdot 10^{-3}$ mols per liter at 25.75°, while Carter [7] gives its solubility as $5.18 \cdot 10^{-3}$ mols per liter at 25°.

The solubility of barium fluoride as a function of the concentration of the

TABLE 1

Solubility of BaF_2 in Solutions of KF and the Values of L_{pBaF_2}, L'_{aBaF_2}, and L''_{aBaF_2}

Test No	Concentration of KF in solution, mols/liter	Solubility of BaF_2, mols/liter	$L_{pBaF_2} \cdot 10^6$	$L'_{aBaF_2} \cdot 10^6$	$L''_{aBaF_2} \cdot 10^6$
1	0.0	$9.23 \cdot 10^{-3}$	3.15	0.985	1.05
2	$5.002 \cdot 10^{-4}$	$9.10 \cdot 10^{-3}$	3.18	0.993	1.06
3	$1.233 \cdot 10^{-3}$	$8.71 \cdot 10^{-3}$	3.03	0.955	1.02
4	$5.028 \cdot 10^{-3}$	$7.75 \cdot 10^{-3}$	3.28	1.01	1.09
5	$7.031 \cdot 10^{-3}$	$7.13 \cdot 10^{-3}$	3.23	0.995	1.07
6	$1.087 \cdot 10^{-2}$	$6.20 \cdot 10^{-3}$	3.36	1.01	1.09
7	$2.081 \cdot 10^{-2}$	$4.36 \cdot 10^{-3}$	3.80	1.05	1.14
8	$2.480 \cdot 10^{-2}$	$3.43 \cdot 10^{-3}$	3.44	0.931	1.02
9	$5.011 \cdot 10^{-2}$	$1.60 \cdot 10^{-3}$	4.55	0.887	1.01
10	$7.256 \cdot 10^{-2}$	$1.13 \cdot 10^{-3}$	6.33	0.925	1.11
11	$1.001 \cdot 10^{-1}$	$7.5 \cdot 10^{-4}$	7.74	0.802	1.05
12	$1.096 \cdot 10^{-1}$	$6.7 \cdot 10^{-4}$	8.24	0.802	1.04
13	$1.507 \cdot 10^{-1}$	$5.4 \cdot 10^{-4}$	12.5	0.818	1.16
14	$2.008 \cdot 10^{-1}$	$4.0 \cdot 10^{-4}$	16.3	0.865	1.12
15	$2.571 \cdot 10^{-1}$	$3.0 \cdot 10^{-4}$	19.9	0.575	1.02
16	$3.325 \cdot 10^{-1}$	$3.0 \cdot 10^{-4}$	35.7	0.650	1.35
17	$5.020 \cdot 10^{-1}$	$2.2 \cdot 10^{-4}$	55.5	0.413	1.17

potassium fluoride is shown graphically in Fig. 3, and on a larger scale in Fig. 4 for low KF concentrations.

As the tabular data and the figures indicate, the solubility of BaF_2 drops rather rapidly as the concentration of KF rises, especially at low concentrations of the latter. But even at a KF concentration of 0.5 mol per liter it is too high from the analytical point of view. With a view to the quantitative examination of the problem of the solubility of barium fluoride at various degrees of excess of potassium fluoride, we began by computing the magnitude of the solubility product from our experimental data; this product could be used as an indication of the degree to which the usual rule of solubility products is applicable to this case. We computed this product from the equation:

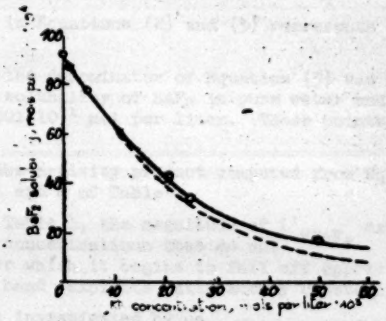

Fig. 4. Solubility of BaF_2 in the $BaF_2 - KF - H_2O$ system at low concentrations of KF.

$$L_{pBaF_2} = C_{BaF_2} \cdot (2C_{BaF_2} + C_{KF})^2 \qquad (1)$$

where C_{BaF_2} and C_{KF} are the concentrations of the fluorides in mols per liter.

The values of L_{pBaF_2} obtained by computation are listed in Column 4 of Table 1.

Inspection of the table shows that the value of L_{pBaF_2} may be considered

fairly constant only up to a KF concentration of 0.01 mol per liter. As the KF concentration is increased still further, the solubility product rises rapidly, even changing its order of magnitude.

Thus, the solubility product rule may be used to precalculate the solubility of BaF_2 when KF is present in excess only when the concentration of the latter is low, not exceeding 0.01 mol/liter.

We also tried to check the applicability of the Debye-Hückel theoretical formula for the activity coefficient of an electrolyte in computing the solubility of BaF_2 when KF is present, as was done for $PbSO_4$ in the papers by I.V.Tananaev and I.B.Mizetskaya [8,9].

We did this by calculating the values of $L_{a_{BaF_2}}$, the constant of the ion activity product, from the experimental values of the solubility of BaF_2 when KF is present.

The computations were made with these formulas:

$$\log L'_{a_{BaF_2}} = \log L_{p_{BaF_2}} - 3.03\sqrt{3C_{BaF_2} + C_{KF}} \qquad (2)$$

and

$$\log L''_{a_{BaF_2}} = \log L_{p_{BaF_2}} - \frac{3.03\sqrt{3C_{BaF_2} + C_{KF}}}{1 + 0.33a\sqrt{3C_{BaF_2} + C_{KF}}} \qquad (3)$$

derived from the thermodynamical equation:

$$L_{p_{BaF_2}} \cdot \gamma^3_{\pm} = L_{a_{BaF_2}}$$

and from the well-known Debye-Hückel formulas for the activity coefficient in the first and second approximations.

The sum under the radical sign in Equations (2) and (3) represents the ionicity of the solution.

The value of the constant a in the denominator of Equation (3) was determined at two experimental points: the solubility of BaF_2 in pure water and in a KF solution with a concentration of $1.001 \cdot 10^{-1}$ mol per liter. These points gave a value of 1.12 Å for a.

The values of the constant of the activity product computed from Equations (2) and (3) are listed in Columns 5 and 6 of Table 1.

As indicated by the figures in Table 1, the magnitude of $L'_{a_{BaF_2}}$ exhibits satsifactory constancy only at KF concentrations that do not exceed approximately 0.05 mol/liter, after which it begins to fall off appreciably. The value of $L''_{a_{BaF_2}}$, on the other hand exhibits satisfactory constancy at all the KF concentrations in the range investigated by us.

Thus, the Debye-Hückel formula for the activity coefficient may be used in its second approximation with sufficient accuracy to precalculate the solubility of BaF_2 at concentrations of KF as high as 0.5 mol per liter.

Using a value of $1.05 \cdot 10^{-6}$ for $L''_{a_{BaF_2}}$ and a = 1.15, we computed the solubility of BaF_2 for several values of C_{KF} from Equation (3), using the method of successive approximations. Our resulting data were used to plot a curve of the variation of C_{BaF_2} with C_{KF}, which is drawn as a solid line in Figs. 3 and 4. The corresponding curves of C_{BaF_2} as a function of C_{KF} on the basis of the solubility product rule have been plotted as dashed lines in these curves for the sake of comparison.

As the figures indicate, the experimental points lie close to the curve plotted from Equation (3). The slight deviations of the experimental points may be attributed to errors in analysis.

The BaF_2 – NaF – H_2O System

The triangular diagram of this system is shown in Fig. 5.

The diagram shows that all the three nodes practically converge at the vertex corresponding to pure BaF_2.

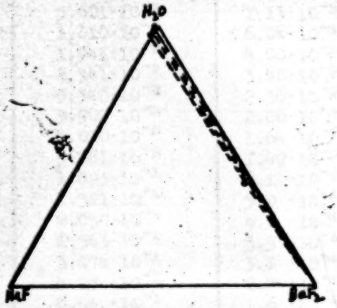

Fig. 5. Composition of the solutions and the moist precipitates in the BaF_2 – NaF – H_2O system in % by weight.

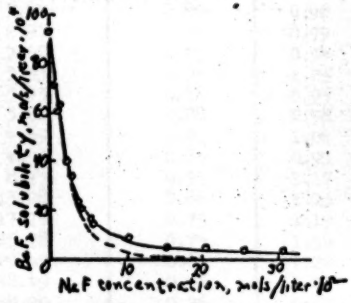

Fig. 6. Solubility of BaF_2 in the BaF_2 – NaF – H_2O system.

In this system, therefore, as in the preceding one, no new solid phases, distinct from BaF_2 and NaF, are formed.

As may be seen from the data in Table 2 and Fig. 6, the variation of the solubility of barium fluoride with the concentration of sodium fluoride resembles that prevailing in the system containing potassium fluoride. It might be added that at the highest concentrations of the alkali metal fluorides the solubility of BaF_2 is systematically somewhat higher when NaF is present than in the presence of KF. There is no doubt that this difference in the BaF_2 solubility would be even more marked at still higher concentrations of KF and NaF. Unfortunately, we were unable to measure the solubility of BaF_2 in more highly concentrated solutions of KF and NaF because of the sharp drop in the accuracy of these determinations when using the method of analysis we had adopted.

As for the preceding system, we computed the values of L_{PBaF_2}, L'_{aBaF_2} and L''_{aBaF_2} from our experimental data on the solubility of BaF_2 when NaF is present. We took the same values for the constant a in the formula for the activity coefficient that had been used in computing L''_{aBaF_2} for the BaF_2 – KF – H_2O system, inasmuch as the changes in the solubility of the BaF_2 follow practically the same course in both instances. The computational results are listed in Table 2.

As the figures in Table 2 indicate, the value of L''_{aBaF_2} exhibits the most satisfactory constancy throughout the investigated range of NaF concentrations.

TABLE 2

Solubility of BaF_2 in Solutions of NaF and the Values of L_{pBaF_2}, L'_{aBaF_2}, and L''_{aBaF_2} at 25°

Test No.	Concentration of NaF in solution, mols/liter	Solubility of BaF_2, mols/liter	$L_{pBaF_2} \cdot 10^6$	$L'_{aBaF_2} \cdot 10^6$	$L''_{aBaF_2} \cdot 10^6$
1	0.00	$9.23 \cdot 10^{-3}$	3.15	0.99	1.05
2	$1.051 \cdot 10^{-4}$	$9.05 \cdot 10^{-3}$	2.99	0.95	1.01
3	$5.112 \cdot 10^{-4}$	$8.89 \cdot 10^{-3}$	2.97	0.94	1.01
4	$1.010 \cdot 10^{-3}$	$8.76 \cdot 10^{-3}$	3.01	0.95	1.02
5	$5.601 \cdot 10^{-3}$	$7.13 \cdot 10^{-3}$	2.81	0.89	0.96
6	$1.010 \cdot 10^{-2}$	$6.04 \cdot 10^{-3}$	2.97	0.92	0.99
7	$1.941 \cdot 10^{-2}$	$4.00 \cdot 10^{-3}$	3.00	0.87	0.94
8	$2.541 \cdot 10^{-2}$	$3.40 \cdot 10^{-3}$	3.53	0.95	1.03
9	$3.340 \cdot 10^{-2}$	$2.36 \cdot 10^{-3}$	3.43	0.84	0.93
10	$3.902 \cdot 10^{-2}$	$2.08 \cdot 10^{-3}$	3.88	0.88	0.98
11	$5.020 \cdot 10^{-2}$	$1.64 \cdot 10^{-3}$	4.69	0.91	1.04
12	$5.281 \cdot 10^{-2}$	$1.42 \cdot 10^{-3}$	4.40	0.83	0.95
13	$1.023 \cdot 10^{-1}$	$8.1 \cdot 10^{-4}$	8.75	0.91	1.17
14	$1.521 \cdot 10^{-1}$	$5.0 \cdot 10^{-4}$	13.28	0.86	1.23
15	$2.050 \cdot 10^{-1}$	$4.2 \cdot 10^{-4}$	17.79	0.75	1.19
16	$2.563 \cdot 10^{-1}$	$3.9 \cdot 10^{-4}$	25.78	0.75	1.32
17	$3.076 \cdot 10^{-1}$	$3.1 \cdot 10^{-4}$	29.45	0.61	1.20
18	$4.23 \cdot 10^{-1}$	$2.7 \cdot 10^{-4}$	48.49	0.52	1.27
19	$6.03 \cdot 10^{-1}$	$1.6 \cdot 10^{-4}$	58.20	0.26	0.89

The variation of the BaF_2 solubility with the NaF concentration is plotted by solid and dashed lines in Fig. 6 according to equations that are analogous to (3) and (1), respectively.

Here, too, the experimental points lie close enough to the solid line.

SUMMARY

1. A study has been made of the equilibrium in the $BaF_2 - KF - H_2O$ and $BaF_2 - NaF - H_2O$ systems at 25°. By use of the Schreinemakers method of analyzing saturated solutions and moist precipitates it was found that neither binary salts nor solid solutions are formed in either system.

2. The 25° isotherm of the solubility of barium fluoride in the $BaF_2 - KF - H_2O$ and $BaF_2 - NaF - H_2O$ systems has been explored as far as a maximum concentration of 0.5 mol/liter of the alkali fluorides.

3. It has been shown that it is possible to make a perfectly satisfactory precalculation of the solubility of BaF_2 in KF and NaF solutions by employing the Debye-Hückel theoretical formula for the activity coefficient in its second approximation, provided the constant a is computed from two experimental points that are not too close together.

In conclusion, I wish to express my sincere gratitude to Prof. I.V.Tananaev for his advice and valued guidance in the performance of this research.

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THE PHYSICO-CHEMICAL ANALYSIS OF TERNARY AQUEOUS SYSTEMS CONSISTING OF FLUORIDES OF THE ALKALI-EARTH METALS AND MAGNESIUM AND FLUORIDES OF THE ALKALI METALS

II. THE TERNARY SYSTEMS: SrF_2-KF-H_2O AND SrF_2-NaF-H_2O AT 25°

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In our preceding report [1] on ternary aqueous systems with BaF_2, KF, and NaF, we pointed out the reasons that led us to engage in a systematic study of the methods of solubility of aqueous systems consisting of difficultly soluble fluorides of the alkali-earth metals and magnesium and fluorides of the alkali metals.

In the present paper we report the results of our investigations of two ternary systems containing strontium fluoride and potassium and sodium fluorides, respectively.

Insofar as we have been able to learn, there is not a single paper in the literature on these systems. Nor has anyone done any research on the binary systems SrF_2 – KF and SrF_2 – NaF. Several authors give figures for the solubility of SrF_2 in pure water, which differ considerably. These discrepancies are apparently due in the main to differences in the original preparations of SrF_2 employed.

EXPERIMENTAL

Constituents. The preparation of the initial solutions of potassium and sodium fluorides has been described in the preceding report. The strontium fluoride was synthesized from chemically pure strontium carbonate and chemically pure hydrofluoric acid. Analysis of the final preparation indicated it contained 99.92% SrF_2.

Procedure. The experimental technique was in the main the same as that used in our investigation of systems containing barium fluoride; it has been described in detail in the previous report [1]. The system's components were mixed together in two different ways, making it possible to approach the state of equilibrium from two opposite directions: from the unsaturated state and from the supersaturated state.

In the first method, used in most of our tests, a small quantity of solid SrF_2 was added to a solution of the alkali fluoride of known titer, after which the system was kept in a thermostat with constant vigorous stirring. In the second method, a certain quantity of a titrated solution of the alkali fluoride was added to a saturated solution of SrF_2 in water, which always contained a slight excess of solid SrF_2 in suspension in it.

To determine whether new solid phases distinct from SrF_2, KF, or NaF, are

generally formed in such systems, we began our experiments with solutions that had the highest concentrations of the alkali fluoride.

In view of the slowness with which equilibrium was reached and of the possibility of the initial solid phase (SrF_2) being converted into a new solid phase, we extended the period of saturation to two months in these instances.

In the cases where the solubility of the SrF_2 was measured (at low concentrations of the alkali fluoride), the required minimum thermostat time for the mixture was found by means of special tests, run to establish a constant SrF_2 concentration in the solution. These tests showed that when a solution of KF or NaF was saturated with solid SrF_2, the concentration of strontium fluoride became constant within 2-3 days, whereas it took 10 days for the concentration of strontium in the solution to become constant when the second method of mixing the components was used.

Samples of the solutions and of the moist precipitates were analyzed as follows to determine their constituents.

The strontium in the solutions was determined by precipitating it as the carbonate, followed by a final acidimetric determination. Gravimetric burets were used in titration. The percentage of the alkali-metal fluorides in the solutions was determined by the sulfate method. When the concentration of the alkali-metal fluoride in the solution was low, its percentage was computed from the data on the composition of the initial mixture of the constituents.

The samples of the moist precipitates were analyzed for their SrF_2 and MeF content by converting the fluorides into sulfates, separating the sulfate of the alkali metal from the strontium sulfate by 50% alcohol, and weighing the $SrSO_4$ and the Me_2SO_4 recovered by evaporating the alcoholic solution. The amount of water in the precipitates was determined by the difference between the weight of the moist precipitate and the amount of SrF_2 + MeF found.*

Test Results and Their Evaluation

1. The SrF_2 – KF – H_2O System

The compositions of some solutions with the highest concentrations of KF and of the corresponding moist precipitates are shown graphically in Fig. 1

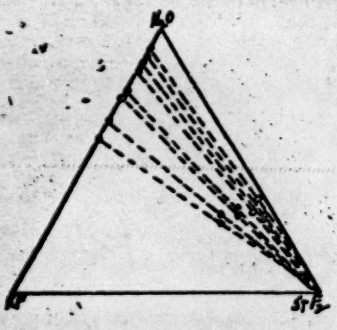

Fig. 1. Compositions of solutions and moist precipitates in the SrF_2 – KF – H_2O system (wt. %).

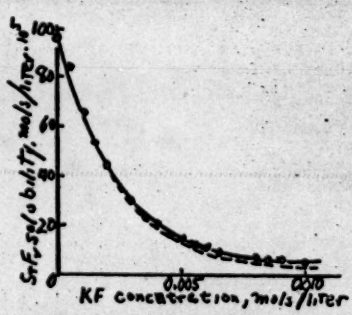

Fig. 2. Solubility of SrF_2 in the SrF_2 – KF – H_2O system.

* In our study of the SrF_2–NaF–H_2O system we also determined the amount of water in the moist precipitates by desiccating the samples to constant weight at 150°.

Inspection of the diagram shows that no binary salts or solid solutions are formed in this system. A certain scattering of the nodes is due to analytical error.

The values of the solubility of strontium fluoride at various concentrations of potassium fluoride are listed in Table 1.

TABLE 1

Solubility of SrF_2 in KF Solutions and Values of $L_{p_{SrF_2}}$ and $L_{a_{SrF_2}}$

Test No.	Concentration of KF in solution, mols/liter	Solubility of SrF_2, mols/liter	$L_{p_{SrF_2}} \cdot 10^9$	$L_{a_{SrF_2}} \cdot 10^9$
1	0.00	$9.62 \cdot 10^{-4}$	3.56	2.46
2	$4.987 \cdot 10^{-4}$	$8.37 \cdot 10^{-4}$	3.97	2.70
3	$9.974 \cdot 10^{-4}$	$6.56 \cdot 10^{-4}$	3.50	2.39
4	$1.496 \cdot 10^{-3}$	$5.38 \cdot 10^{-4}$	3.56	2.41
5	$1.995 \cdot 10^{-3}$	$4.46 \cdot 10^{-4}$	3.72	2.48
6	$2.494 \cdot 10^{-3}$	$3.67 \cdot 10^{-4}$	3.82	2.51
7	$2.992 \cdot 10^{-3}$	$2.92 \cdot 10^{-4}$	3.74	2.42
8	$3.421 \cdot 10^{-3}$	$2.36 \cdot 10^{-4}$	3.91	2.48
9	$3.990 \cdot 10^{-3}$	$2.05 \cdot 10^{-4}$	3.98	2.48
10	$4.488 \cdot 10^{-3}$	$1.64 \cdot 10^{-4}$	3.79	2.31
11	$4.987 \cdot 10^{-3}$	$1.44 \cdot 10^{-4}$	4.00	2.39
12	$5.487 \cdot 10^{-3}$	$1.19 \cdot 10^{-4}$	3.89	2.30
13	$5.985 \cdot 10^{-3}$	$1.09 \cdot 10^{-4}$	4.19	2.40
14	$6.485 \cdot 10^{-3}$	$9.1 \cdot 10^{-5}$	4.06	2.28
15	$7.982 \cdot 10^{-3}$	$6.8 \cdot 10^{-5}$	4.45	2.37
16	$8.480 \cdot 10^{-3}$	$6.4 \cdot 10^{-5}$	4.71	2.46
17	$8.948 \cdot 10^{-3}$	$5.6 \cdot 10^{-5}$	4.58	2.36
18	$9.877 \cdot 10^{-3}$	$5.1 \cdot 10^{-5}$	5.16	3.56

The value for the solubility of SrF_2 in pure water found by us is fairly close to the figure obtained by Kohlrausch [3] ($9.45 \cdot 10^{-4}$ mol per liter at 18°), but it is quite out of line with Carter's value [4] ($3.11 \cdot 10^{-4}$ at 25°).

The variation of the solubility of strontium fluoride with the concentration of potassium fluoride is shown graphically in Fig. 2.

The foregoing data and Fig. 2 indicate that the solubility of SrF_2 drops uninterruptedly as the KF concentration rises.

To check the applicability of the solubility product rule in this case we computed the value of $L_{p_{SrF_2}}$ from our experimental data, from the formula:

$$L_{p_{SrF_2}} = C_{SrF_2} \cdot \left(2C_{SrF_2} + C_{KF}\right)^2 . \qquad (1)$$

The calculated values of $L_{p_{SrF_2}}$ are given in Table 1.

The figures in Table 1 show that $L_{p_{SrF_2}}$ remains approximately constant only up to a KF concentration of 0.006 mol per liter, after which it begins to rise noticeably. If we take as the value of $L_{p_{SrF_2}}$ the figure of $3.57 \cdot 10^9$, computed from the observed solubility of SrF_2 in pure water, and then calculate the solubility of SrF_2 at various concentrations of potassium fluoride from Equation (1), we get the function shown in Fig. 2 by the dashed line.

The same graph indicates that the experimental values of the SrF_2 solubility differ from those computed by the solubility product rule by an amount

that considerably exceeds the effect of experimental errors.

To ascertain whether it was possible to precalculate the solubility of SrF_2 from the thermodynamic law of the constancy of the activity products, using the Debye-Hückel theoretical equations for the activity coefficient, we computed the values of La_{SrF_2}, the constant of the activity products, from our experimental data. The final equation for computing La_{SrF_2}, using the limiting Debye-Hückel law for the activity coefficient, looks like this:

$$\log La_{SrF_2} = \log C_{SrF_2} + 2 \log (2C_{SrF_2} + C_{KF}) - 3.03 \sqrt{3C_{SrF_2} + C_{KF}}, \qquad (2)$$

where C_{SrF_2} and C_{KF} are the concentrations in mols per liter.

The values of La_{SrF_2} computed from this equation are listed in Column 5 of Table 1.

As these figures show, the values of the constant La_{SrF_2} exhibit satisfactory constancy.

The solid curve plotted in Fig. 2 expresses the solubility of SrF_2 as a function of KF in accordance with Equation (2) when $La_{SrF_2} = 2.46 \cdot 10^{-9}$. The same figure indicates that the experimental points lie on the computed curve throughout the investigated range of KF concentrations.

2. The SrF_2 – NaF – H_2O System at 25°

The composition of the two solutions with the highest NaF concentrations, and of the corresponding wet precipitates, are shown in the ternary diagram of Fig. 3.

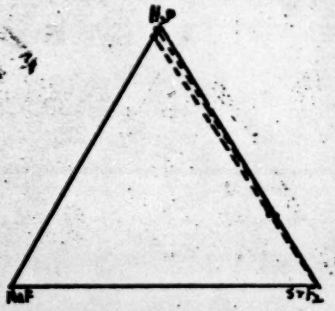

Fig. 3. Composition of solutions and moist precipitates in the SrF_2 – NaF – H_2O system (% by weight).

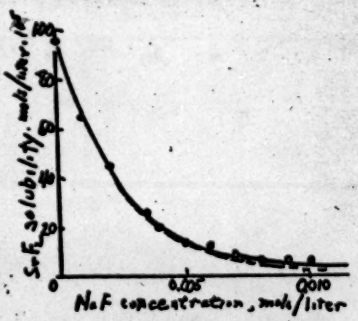

Fig. 4. Solubility of SrF_2 in the SrF_2 – NaF – H_2O system.

Inspection of the diagram shows that both nodes coincide with the vertex that corresponds to pure SrF_2. Hence, no new solid phases, distinct from SrF_2 or NaF, are formed in this system either.

The values for the solubility of strontium fluoride in NaF solutions observed by us are listed in Table 2 and plotted in Fig. 4.

As an inspection of Fig. 4 indicates, the solubility of strontium fluoride as a function of the NaF concentration has the same shape as in the previous

system, containing potassium fluoride. This similarity of the curves is not unexpected, when we remember that the solubility of SrF_2 was measured only for dilute solutions of potassium and sodium fluorides.

The values of $L_{p_{SrF_2}}$ and $L_{a_{SrF_2}}$, computed from the experimental data by means of equations resembling (1) and (2), are listed in Teble 2.

TABLE 2

Solubility of SrF_2 in NaF Solutions and Values of $L_{p_{SrF_2}}$ and $L_{a_{SrF_2}}$ at 25°

Test No.	Concentration of NaF in solution, mols/liter	Solubility of SrF_2, mols/liter	$L_{p_{SrF_2}} \cdot 10^8$	$L_{a_{SrF_2}} \cdot 10^8$
1	0.00	$9.62 \cdot 10^{-4}$	3.56	2.46
2	$9.974 \cdot 10^{-4}$	$6.50 \cdot 10^{-4}$	3.45	2.37
3	$1.995 \cdot 10^{-3}$	$4.51 \cdot 10^{-4}$	3.79	2.54
4	$3.447 \cdot 10^{-3}$	$2.53 \cdot 10^{-4}$	3.97	2.52
5	$3.990 \cdot 10^{-3}$	$2.00 \cdot 10^{-4}$	3.86	2.41
6	$4.987 \cdot 10^{-3}$	$1.40 \cdot 10^{-4}$	3.87	2.31
7	$5.985 \cdot 10^{-3}$	$1.19 \cdot 10^{-4}$	4.61	2.64
8	$6.982 \cdot 10^{-3}$	$9.3 \cdot 10^{-5}$	4.77	2.63
9	$7.980 \cdot 10^{-3}$	$6.6 \cdot 10^{-5}$	4.35	2.31
10	$8.982 \cdot 10^{-3}$	$6.4 \cdot 10^{-5}$	5.29	2.71
11	$9.978 \cdot 10^{-3}$	$6.0 \cdot 10^{-5}$	6.11	3.03
12	$1.096 \cdot 10^{-2}$	$5.0 \cdot 10^{-5}$	6.16	2.95

As these figures indicate, here again the value of $L_{a_{SrF_2}}$ remains satisfactorily constant, in contrast to $L_{p_{SrF_2}}$, which rises nearly 100% when the NaF concentration is varied from 0 to 0.01 mol per liter.

The solid and dashed curves plotted in Fig. 4 show how the solubility of SrF_2 changes according to Equations (2) and (1). Here, too, the experimental points likewise lie on the solid curve.

SUMMARY

1. A study has been made of the equilibria in the $SrF_2 - KF - H_2O$ and $SrF_2 - NaF - H_2O$ systems at 25°. A Schreinemakers analysis of the saturated solutions and moist precipitates showed that no binary salts or solid solutions are formed in either system.

2. The isotherms of the solubility of SrF_2 in the $SrF_2 - KF - H_2O$ and $SrF_2 - NaF - H_2O$ systems at 25° have been investigated at concentrations of alkali fluorides ranging from 0 to 0.1 mol per liter. The isotherms are identical in both cases.

3. It has been shown that it is possible to precalculate the solubility of strontium fluoride in solutions of KF and NaF of various concentrations not exceeding 0.01 mol per liter, by using the limiting Debye-Hückel formula for the activity coefficient.

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*See CB translation previous article.

ABSORPTION SPECTRA OF SOLUTIONS OF ORGANIC DYESTUFFS AND MINERAL SALTS IN THE RED REGION

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In recent years the method of standard series and scales has become one of the widely used colorimetry methods.

The instability of scales prepared with solutions of organic dyes has stimulated a search for colored solutions of mineral salts that could imitate the colors of organic dyestuffs while being more stable.

The first effort to substitute solutions of mineral salts for organic dyestuffs was made by Windisch [1], who proposed to imitate the Michaelis monochromatic indicators by solutions of potassium chromate and bichromate. Windisch's research was continued by Kolthoff [2], who set forth recipes for imitating the colors of these indicators: neutral red, methyl orange, and tropeolin 00. In his imitations he employed $FeCl_3 \cdot 6H_2O$ and $Co(NO_3)_2$ solutions as well as a mixture of $KMnO_4$ and $K_2Cr_2O_7$ in H_2SO_4, but the latter solutions proved to be unstable. In 1927, A. Taub [3] described new standard solutions prepared from mixtures of the following salts:

$CoCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, and $CuCl_2 \cdot 2H_2O$.

The colors of these solutions remained the same for 10 years.

In 1937, K.V.Flerov [4] employed permanent, nonfading scales for other analytical purposes as well. Using solutions of inorganic salts of the heavy metals and combinations thereof, namely:

$FeCl_3 \cdot 6H_2O$; $CuSO_4 \cdot 5H_2O$; $Cu(CH_3COO)_2$; $CuCl_2 \cdot 2H_2O$; $NiSO_4$; $CoCl_2 \cdot 2H_2O$; $Co(CH_3COO)_2$; and $K_2Cr_2O_7$,

Flerov secured 23 basic tones of Ostwald's 24 charts of color tones.

Using this method, K.V.Flerov and his co-workers developed various procedures, namely: the colorimetric determination of iron (Velichkovskaya [5]); of lead (Ozimov and Krasnov [6]); and of the hydrogen-ion concentration (Flerov and Ozimov [7]).

When the color of the mineral-salt solutions is the same as that of the organic dyestuffs, it may be supposed that both solutions will have the same absorption spectra. The first research work on the comparison of the absorption spectra of organic dyestuffs and mineral salts was done by A. Jahnke and Kropacsy [8], who investigated the spectra of $FeCl_3 \cdot 6H_2O$ and $Co(NO_3)_2$ solutions, which imitated the color of neutral red, methyl orange, and tropeolin 00 at various pH values, as well as K_2CrO_4 and $K_2Cr_2O_7$ solutions, which imitated the color of dinitrophenol and nitrophenol. Their research was done by the visual method, using

Schott colorimetric jars and a Zeiss spectroscope. According to the authors, not enough work was done on the absorption spectra in the red region, owing to their instrument's low sensitivity in that region. Mellon [9] investigated the absorption spectra of some mineral solutions.

EXPERIMENTAL

It was the objective of this research to find out how the absorption spectra of the standards we had prepared compared with the absorption spectra of organic dyestuffs employed in Bogen's universal indicator. We did this by investigating 5 samples of buffer solutions with the following pH values: 2.4, 2.6, 2.8, 3.0, and 3.2 (the whole red region covered by Bogen's indicator*). Each pH value was represented by three solutions:

1) 10 ml of a buffer solution with 10 drops of Bogen's indicator (drop volume = 0.025 ml); the buffer solution was prepared by the Clark and Leibs method, the pH of this solution being determined electrometrically with a hydrogen electrode;

2) A standard solution consisting of a mixture of $CoCl_2 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$, prepared as specified below and selected visually, with an optical comparator, to agree with the color of the buffer solution;

3) A standard solution consisting of a mixture of $CoCl_2 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$, prepared as specified below and selected by means of a compensating photocolorimeter to agree with the color of the buffer solution.

The following solutions: ferrous chloride – $FeCl_2$ – 0.0071370 g/ml; and cobalt chloride – $CoCl_2$ – 0.070325 g/ml, were used to imitate the color of Bogen's indicator in the buffer solutions.

The solutions of ferrous chloride and cobalt chloride were prepared with a 5% solution of hydrochloric acid to prevent hydrolysis.

The amount of the ferrous chloride and cobalt chloride solutions required to imitate the color of Bogen's indicator is given in the subjoined Table 1.

TABLE 1

Serial No.	pH	Optical comparator			Compensating photocolorimeter			Total volume, ml
		$FeCl_3$	$CoCl_2$	H_2O	$FeCl_3$	$CoCl_2$	H_2O	
		Quantity, ml						
1	2.4	0.15	1.60	0.25	0.14	1.62	0.24	2
2	2.6	0.25	1.50	0.25	0.22	1.35	0.43	2
3	2.8	0.35	1.40	0.25	0.32	1.28	0.40	2
4	3.0	0.40	1.20	0.40	0.53	1.31	0.16	2
5	3.2	0.20	1.00	0.20	0.82	0.91	0.27	2

These samples were given names (Table 2).

TABLE 2

Serial No.	pH	Volume	Buffer solution	Standard solution, selected visually	Standard solution, selected photocolorimetrically
			Designations		
1	2.4	10	1 B	1 V	1 Ph-E
2	2.6	10	2 B	2 V	2 Ph-E
3	2.8	10	3 B	3 V	3 Ph-E
4	3.0	10	4 B	4 V	4 Ph-E
5	3.2	10	5 B	5 V	5 Ph-E

*Bogen's indicator consists of the following indicators: phenolphthalein, methyl red, dimethylaminoazobenzene, bromothymol blue, and thymol blue.

The absorption spectra of these solutions were measured with the Koenig-Martens spectrograph in the following wavelength ranges:

1 B,	1 V,	1 Ph-E	from 6900 to 5500 A
2 B,	2 V,	2 Ph-E	
3 B,	3 V,	3 Ph-E	
4 B,	4 V,	4 Ph-E	
5 B,	5 V,	5 Ph-E	from 6900 to 5100 A

The last sample was measured over a larger interval because the red begins to change to orange at a pH of 3.2.

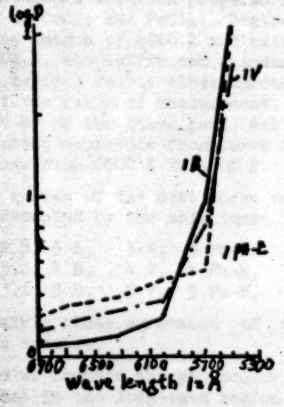

Fig. 1

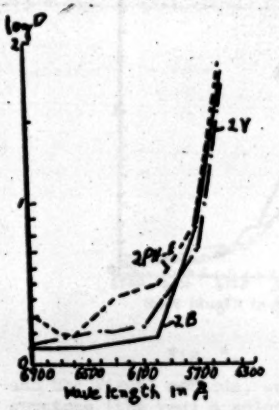

Fig. 2.

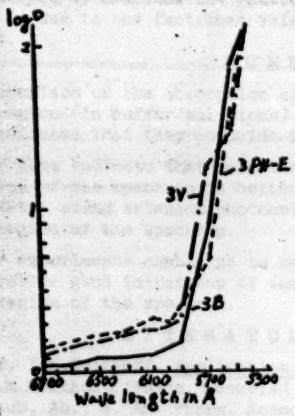

Fig. 3

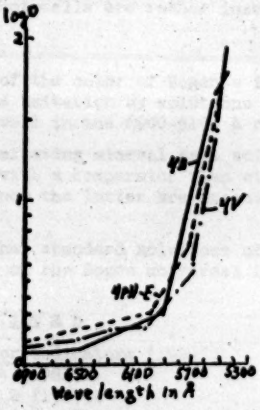

Fig. 4

The optical densities are given for a 20-mm column and are represented by the absorption spectra curves of the buffer with Bogen's indicator and of two standard solutions of mineral salts imitating the color of Bogen's indicator in this respect (Figs. 1, 2, 3, 4, and 5). Each value is the mean of 3 samples.

Investigating the absorption-spectra curves of solutions 1 B, 1 V, and 1 Ph-E at a pH ≠ 2.4 leads to the following conclusion: in the long-wave portion of the spectrum, from 6900 Å to 5900 Å, the buffer solution colored with Bogen's indicator exhibits greater absorption than the standard solution prepared from a mixture of $CoCl_2$ and $FeCl_3$. Beginning at the wave length of 6000 Å and extending to 5500 Å, the buffer and standard solutions exhibit fairly close agreement throughout the range of measurement. Curve 2 Ph-E, on the other hand, exhibits a rather sharp departure from Curve 2 B in the range from 6500 Å to 5700 Å.

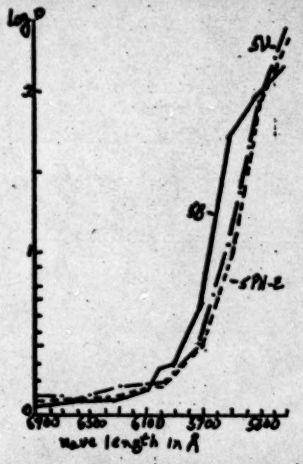

Fig. 5.

The curves of the next three samples, represented by the solutions:

pH = 2.8 3 B, 3 V, 3 Ph-E,
pH = 3.0 4 B, 4 V, 4 Ph-E,
pH = 3.2 5 B, 5 V, 5 Ph-E,

exhibit fairly close agreement of the absorption spectra.

When we compare the photocolorimetric and the visual methods, we must bear in mind that in the long-wave region of the spectrum (the red) a solution selected visually yields greater agreement with the color of the buffer than the solution selected by means of the photocolorimeter, as is seen in all the 5 samples. This is due to the fact that selenium photocells are rather insensitive to red light.

SUMMARY

1. Comparison of the absorption spectra of the color of Bogen's indicator in the red region (in buffer solutions) and its imitation by solutions of $CoCl_2$ and $FeCl_3$ indicated that they coincide fairly well in the 6900-5100 Å range.

2. Our data indicate that selecting an imitating mineral salt solution in the red region of the spectrum is better done with a comparator than with a photocolorimeter using selenium photocells, since the latter are insensitive in the red region of the spectrum.

3. Our experiments enable us to assume that standard solutions of $CoCl_2$ and $FeCl_3$ provide good imitations of the color of the Bogen universal indicator in the red region of the spectrum.

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ULTRAVIOLET ABSORPTION SPECTRA OF SOME HETEROCYCLIC COMPOUNDS IN THE PRESENCE OF AN ALKALI

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In our efforts to ascertain the mechanism of the photosensitizing action of some dyes, their ultraviolet absorption spectra have been the object of research. It has been shown [1] that a combination of the radicals of two heterocycles: rhodanine (or N-phenylrhodanine) and benzothiazole, besides retaining their usual absorption in the bands typical of the initial heterocycles, exhibit two new and extremely intensive bands – one in the long-wave section and the other in the short-wave section of the ultraviolet. Apparently, there are three absorption centers in the combination products: the heterocyclic radicals by themselves and their combination product as a whole. This was likewise indicated by the effect of alkalies upon the absorption of some photosensitizing dyes. Thus, the absorption of an alkaline solution of 5-[3-ethyl-2,3-dihydrobenzothiazolidene-(2)]-rhodanine (Dye I) changes only in the middle of the ultraviolet, i.e., in the region of the bands that are typical of heterocyclic radicals, compared to a neutral alcoholic solution, whereas the presence of an alkali causes merely a slight diminution in the intensity of absorption in the region of the bands that are characteristic of the coupling product as a whole. We had to check whether the changes occurring in the middle portion of the absorption curve of the given dye as the result of the alkali's action resemble the changes in the absorption curves of the original heterocycles.

As had been found earlier [2], the presence of an alkali has no apparent effect upon the absorption curve of benzothiazole. Significant changes occur in rhodanine and N-phenylrhodanine, however.

Rhodanine was investigated in alcoholic solutions of 10^{-2} -10^{-4} molar concentration, with 1000 molecules of sodium alcoholate present per molecule of rhodanine. The results of measurement are listed in Table 1. The absorption curve for a solution with a 10^{-2} molar concentration (Fig. 1, Curve 2) begins at $\lambda = 4550$ A and, rising upward, forms a wide band with a maximum at $\lambda = 3900$ A and $\varepsilon = 55$. After a shallow minimum at $\lambda = 3620$ A and $\varepsilon = 30$, the curve again rises, ending at $\lambda = 3240$ A.

In the solution with a 10^{-3} molar concentration, the absorption curve (Fig. 1, Curve 3) begins at $\lambda = 3780$ A and rises steeply to $\lambda = 3660$ A. In the short-wave section, the curve exhibits a deep minimum at $\lambda = 2665$ A and $\varepsilon = 200$.

In the solution with a 10^{-4} molar concentration, absorption begins (Fig. 1, Curve 3) at $\lambda = 3530$ A; it rises steeply and exhibits a narrow band with a maximum at $\lambda = 3440$ A and $\varepsilon = 5000$ and a wide band with a maximum at $\lambda = 2955$ A

and ε = 13000. In the longwave region the latter band has a clearly marked point of inflection between 3260 and 3170 Å; the two minima of the curve are located at λ = 3330 Å and ε = 3000 and λ = 2655 Å and ε = 200.

Table 2 gives the data on the absorption-band maxima of rhodanine in alcohol [3] and in alcohol with an excess of sodium alcoholate present.

As the table data and Fig. 1 indicate, the presence of an alkali causes a significant change in the absorption curve of rhodanine, namely:

a) in alkaline solutions the end and the beginning of absorption do not coincide when the solution is diluted with alcohol, in contrast to neutral alcoholic solutions;

TABLE 1

Rhodanine in Alcohol, 10^{-2} - 10^{-4} molar, with 1000 molecules of sodium alcoholate

λ		ε	λ		ε
4500		10	3400	maximum	5000
4100		40	3400		4000
4000		50	3360		3500
3900	maximum	55	3330	minimum	3000
3800		50	3300		3500
3680		35	3260		5000
3620	minimum	30	3170		7000
3560		35	3110		10000
3240		100	2955		13000
3780		100	2800		10000
3660		1000	2620		1000
2780		1000	2250	maximum	1000
2670		250	2200		1600
2655		200			
2640		250			
2470		1000			
3530		1000			
3480		4000			

b) The action of the alkali produces a noticeable shift of the whole absorption curve toward the longer wavelengths; two new bands make their appearance at λ = 3900 and 3440 Å.

c) The longwave band of rhodanine in neutral alcohol, located at λ = 2950 Å

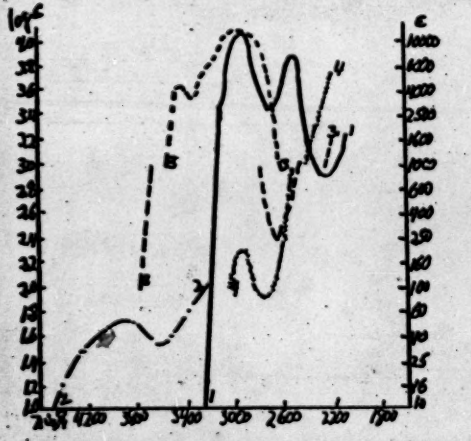

Fig. 1

1-Rhodanine in alcohol, 10^{-2}-10^{-4} molar; 2-rhodanine in alcohol, 10^{-2} molar, with 1000 molecules of C_2H_5ONa; 3-rhodanine in alcohol, 10^{-3}-10^{-4} molar, with 1000 molecules of C_2H_5ONa 4-rhodanine in alcohol, 10^{-3}-10^{-4} molar, with 1000 molecules of C_2H_5ONa after standing for a day.

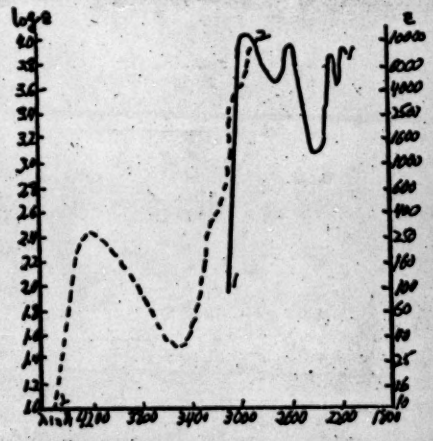

Fig. 2

1-N-phenylrhodanine in alcohol, 10^{-3} to 10^{-4} molar 2-N-phenylrhodanine in alcohol, 10^{-2} to 10^{-4} molar, with 1000 molecules of C_2H_5ONa.

Point of inflection

TABLE 2

Compound	Band maximum at: 1		2		3		4		5	
	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
Rhodanine in alcohol	–	–	–	–	–	–	2950	10000	2515	7000
Ditto + 1000 molecules of C_2H_5ONa	3900	50	Inflection 3260-3170	5000-7000	3440	5000	2955	13000	–	–

and ε = 10 000, is retained in the presence of sodium alcoholate. But in the alkali this band is widened considerably, as the result, apparently, of both the shift of its longwave region toward the longer wavelengths due to the action of the alkali and of the fact that the rhodanine band in neutral alcohol, with a maximum at λ = 2515 A and ε = 7000 falls within this region as it shifts toward the longer wavelengths (in the alkali a deep minimum coincides with the maximum of this band). This displacement of the longwave region is considerable: 560 A at ε = 100, for example, and 400 A at ε = 1000.

The reason for the above changes in the absorption curve of rhodanine when alkali is present in 10^{-3} and 10^{-4} molar solutions may well be its enolization, with the ensuing formation of a salt. We know that rhodanine can form a salt with various metals in alkaline media [4]. This is explained by the enolization of the rhodanine. The formation of a salt facilitates the displacement of absorption toward the longer wavelengths, as is the case with other enols [5]. The shift of the equilibrium between the enol and the rhodanine toward the latter might explain the failure of the beginning and the end of absorption to coincide, observed when the solution is diluted.

It is noteworthy that the absorption of rhodanine in 10^{-3} and 10^{-4} molar solutions with 1000 molecules of sodium alcoholate present undergoes a marked change after standing for one day. In this case, the curve (Fig. 1, Curve 4) begins at λ = 3050 A and rises, exhibiting only one narrow band with a maximum at λ = 2945 A and ε = 250; after a shallow minimum, the curve resumes its rise and comes to an end at λ = 2200 A. The bands observed in freshly prepared solutions are not present, with the exception of the basic rhodanine band at 2950 A, which suffers a sharp drop in intensity (about fiftyfold). The absorption curves of these solutions after being allowed to stand for a day look like continuations of the curve for the 10^{-2} molar solution.

TABLE 3

N-phenylrhodanine in alcohol, 10^{-2} to 10^{-4} molar, with 1000 molecules of sodium alcoholate

λ		ε	λ		ε
4500		10	3460		35
4250		250	3250		300
4150	Maximum	300	3160	Point of inflection	500
4050		250	3070		3000
3550		35	2980	Point of inflection	6000
3505	Minimum	30	2860		10000

We investigated the absorption of N-phenylrhodanine in 10^{-2} to 10^{-4} molar alcoholic solutions with 1000 molecules of sodium alcoholate present per molecule of the substance. The measurement data are given in Table 3. The absorption

curve (Fig. 2, Curve 2) begins at λ = 4500 Å and rises steeply, forming a wide band with a maximum at λ = 4150 Å and ε = 300; the curve resumes it rise, after a minimum at λ = 3505 Å and ε = 30, to λ = 2860 Å; there are two inflections along this rise: between 3250 and 3160 Å (ε - 500 and 300) and 3070 and 2980 Å (ε - 6000 and 3000).

Comparison of the absorption curves of N-phenylrhodanine in alcohol and in alcohol with sodium alcoholate present (Fig. 2, Curves 1 and 2, respectively) indicates that the alkali causes: a) the appearance of a new wide band, as in the case of rhodanine, with a maximum at λ = 4150 Å – in the case of rhodanine this band is located at λ = 3900 Å and is only one-fifth as intense as the N-phenylrhodanine band; and b) the appearance of a point of inflection between 3250 and 3160 Å, as in the case of rhodanine – with the latter this inflection is located at much higher values of ε. As for the rest, the effect of the alkali upon the absorption of N-phenylrhodanine differs markedly from its influence upon the rhodanine absorption curve. The noticeable shift of the absorption curve toward the longer wavelengths observed in freshly prepared 10^{-3} to 10^{-4} molar alkaline solutions of rhodanine does not occur with N-phenylrhodanine. Nor do the beginning and the end of absorption fail to coincide when N-phenylrhodanine is diluted. The λ= 2950 Å band, which is not displaced but is noticeably widened when alkali acts upon rhodanine, loses some of its intensity with N-phenylrhodanine and is manifested merely as a point of inflection between 3070 and 2980 Å.

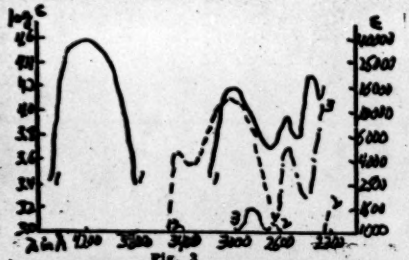

Fig. 3

1-5-[3-ethyl-2,3-dihydrobenzothiazolidene-(2)]-rhodanine in alcohol, $4 \cdot 10^{-5}$ molar, with 1000 molecules of C_2H_5ONa; 2-rhodanine in alcohol, 10^{-4} molar, with 1000 molecules of C_2H_5ONa; 3-benzothiazole in alcohol, 10^{-4} molar, with 1000 molecules of C_2H_5ONa.

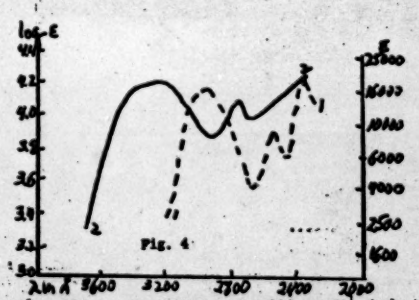

Fig. 4

1-5-[3-ethyl-2,3-dihydrobenzothiazolidene-(2)]-rhodanine in alcohol, $4 \cdot 10^{-5}$ molar, with 1000 molecules of C_2H_5ONa; 2-5-[3-ethyl-2,3-dihydrobenzothiazolidene-(2)-ethylidene]-rhodanine in alcohol, $4 \cdot 10^{-5}$ molar, with 1000 molecules of C_2H_5ONa.

Table 4 gives the data on the maxima of the absorption bands for benzothiazole [2], rhodanine, and dyestuffs [1] in alcoholic solutions with an excess of sodium alcoholate present.

TABLE 4

Compound	Band maxima at:											
	1		2		3		4		5		6	
	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
Dye I in alcohol	4215	50000	–	–	–	–	2770	20000	2620	20000	2340	25000
Ditto in alkali	4200	25000	–	–	2985	15000	–	–	2560	8750	2380	17500
Rhodanine in alkali	3900	50	3440	5000	2955	13000	–	–	–	–	–	–
Benzothiazole in alkali ..	–	–	–	–	–	–	2835	1600	2545	5000	–	–

As is seen in the data of Table 4, and in the curves plotted in Fig. 3, the changes in the absorption curve for Dye I due to the presence of an alkali basically resemble those occurring with rhodanine. The curve for the dye in alkali consists as it were of two groups of bands: 1) highly intense bands with maxima at λ = 4200 and 2380 A, which are characteristic of the coupling products of two heterocycles and of a neutral alcoholic solution; and 2) bands that are characteristic of rhodanine in alkali (with a maximum at λ = 2955 A) and of benzothiazole in alkali (with a maximum at 2545 A). In the dyestuff, the latter two bands exhibit a slightly higher intensity. The other rhodanine and benzothiazole bands do not appear on the dyestuff curve, owing to the superposition of the more intense absorption bands. Evidently, a few independent absorption centers occur in the alkaline solution for the dyestuff, too: the rhodanine and benzothiazole radicals, as well as their coupling product as a whole. The absorption curve appears to be the result of the superposition of the absorption bands that are characteristic of each of the above-mentioned absorption centers, considered separately.

This is also manifested by 5-[3-ethyl-2,3-dihydrobenzothiazolidene-(2)-ethylidene]-rhodanine (Dye II) in alkaline solution. Its absorption curve with sodium alcoholate present [1] differs from that of Dye I (Fig. 4) solely in that all the absorption bands are shifted nearly parallel toward the longwave region. Evidently, the presence of two methenyl groups between the two heterocycles promotes a greater bathochrome effect of the alkali.

SUMMARY

1. The absorption curves of rhodanine and N-phenylrhodanine in alcoholic solutions of sodium alcoholate have been plotted.

2. It has been found that in alkaline as well as in neutral alcoholic solutions the absorption curves of the coupling products of these heterocycles are the result of superposition of the absorption bands that are characteristic of the individual heterocycles and of their coupling product as a whole.

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CHANGES IN DENSITY IN HOMOLOGOUS SERIES OF ORGANIC COMPOUNDS

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The direct corrolaries of Kopp's statement (1842) on the additivity of molar volume, V, were: the constancy of the homologous difference of molar volume, ΔV; its independence of the nature of the functional group; and the linear relationship between the value of V and the molecular weight of the number of carbon atoms, n, in the hydrocarbon chain. Yet, in spite of more than 100 years of research, we have been unable to discover a strictly linear relationship between V and n at any comparison temperature whatsoever [1]. Even Lossen [2] pointed out that V rises faster than n and proposed a formula in which n is raised to the second power for some homologous series. In 1915 Le Bas proposed a parabolic formula for computing the changes in V in the homologous series of saturated hydrocarbons. Nor were the expressions for V as a function of n proposed by Kauffmann [3], Egloff and Kuder [4], and others any simpler. It was also found that ΔV depends on the nature of the functional group, increasing in the homologous series as the number of carbon atoms in the hydrocarbon chain rises [5]. It was established that ΔV varies more rapidly in the lower members of the homologous series than in the higher members, evidently approaching some limiting value as an asymptote [6]. The reason for the absence of strict additivity of the molar volume may be found by considering the nature of the changes in density in homologous series.

Fig. 1 gives curves showing the density changes in 19 homologous series [7]. They confirm the view [6] that the density approaches some asymptotic value as the number of carbon atoms in the hydrocarbon chain is increased, and that all homologous series may be classified into three groups: rising, falling, and nearly stable series, insofar as density changes are concerned.

The nature of these curves enables us to propose the following formula for computing density in homologous series:

$$d_n = d_{lim.} \frac{bn}{bn + 1}, \qquad (1)$$

where d_n is the density of the series member with n carbon atoms in the normal hydrocarbon chain; $d_{lim.}$ is the ultimate density for the given series; and b is a constant.

The values of $d_{lim.}$ and b may be computed for each series from the data for $\frac{1}{b \cdot d_{lim.}}$ and $\frac{1}{d_{lim.}}$, which in turn are found by plotting n/d versus n. The values of $d_{lim.}$ and b for some homologous series are given in Table 1. As these figures show, both $d_{lim.}$ and b change appreciably with the nature of the functional group.

The observed [8] values of the density of members of these four homologous series are listed in Table 2, together with the values computed from Equation (1). The discrepancies are less than 0.5%, except in the first two or three members of each series. They usually range between 0.00% and 0.25%, i.e., they are less

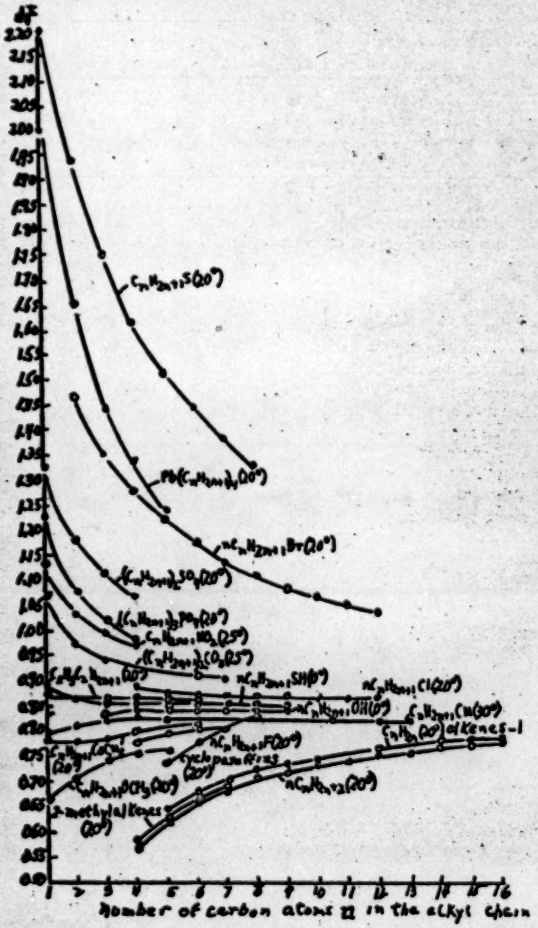

Fig. 1. Density isotherms.

than when computed by many other formulas, such as those advanced by Kauffman [3], Egloff and Kuder [4], and others.

The tendency of the density to approach an asymptotic value in homologous series is apparently due to the fact that the introduction of the CH_2 group into the hydrocarbon chain tends to increase as well as to lower the density. Actually, we know that (except for the first few members of the series) the dipole moment undergoes absolutely no significant change as the number of CH_2 groups in the chain is increased; nor does the form of the molecule change in most instances. As the chain is lengthened, the mass of the molecule rises first of all, since the density is a product of the molecular mass, m, and n, the number of such molecules per unit volume, this ought to contribute to an increase in the density of the compound formed. On the other hand, the size of the molecule rises as the chain grows longer (the length increases by 1.2 to 1.3 Å for each CH_2 group), which results in a diminution of their number per unit volume, and hence in a decrease in the density of the compound.

TABLE 1

Homologous series	Temp.	$d_{lim.}$	b
Normal hydrocarbons	20°	0.8665	+ 0.5351
Thio alcohols....	25	0.8420	+41.813
Normal alcohols..	0	0.8527	+ 7.230
Fatty acids	20	0.877	- 4.486

If the number of molecules per unit volume did not change as the number of CH_2 groups in the hydrocarbon chain increased, the density of the resulting compound would be proportional to the resulting relative growth of the molecular weight:

$$d'_{n+1} = \frac{M_{n+1}}{M_n} \cdot d_n ,$$

where d_n and M_n are the density and the molecular weight, respectively, of a

TABLE 2

$C_nH_{2n+1}X$	X = H	(20°)	X = Sh	(25°)	X = OH	(0°)	X = COOH	(20°)
n =	Comput.	Observ.	Comput.	Observ.	Comput.	Observ.	Comput.	Observed
1	–	–	0.82229	0.85691	0.74911	0.80999	1.140	1.049
2	–	–	0.83198	0.83147	–	–	0.997	0.992
3	–	–	0.83522	0.83673	0.81514	0.82135	0.959	0.959
4	–	–	0.83734	0.83750	0.82422	0.82393	0.939	0.942
5	0.63055	0.62638	0.83795	0.83750	0.82977	0.82963	0.927	0.929
6	0.66053	0.65942	0.83863	0.83826	0.83350	0.83336	0.922	0.922
7	0.68375	0.68375	0.83905	0.83891	0.83601	0.83634	0.916	0.910
8	0.70229	0.70283	0.83947	0.83956	0.83865	0.83848	0.912	0.907
9	0.71728	0.71790	0.83972	0.84015	0.83976	0.84002	–	–
10	0.72985	0.72985	–	–	–	–	–	–
11	0.7406	0.7404	–	–	–	–	–	–
12	0.7496	0.7493	–	–	–	–	–	–
13	0.7575	0.7568	–	–	–	–	–	–
14	0.7644	0.7636	–	–	–	–	–	–
15	0.7704	0.7688	–	–	–	–	–	–
16	0.7758	0.7749	–	–	–	–	–	–

compound with n carbon atoms in its hydrocarbon chain; d_{n+1} and M_{n+1} are the respective figures for a compound with n+1 carbon atoms. Inasmuch as an increase in the size of the molecule diminishes the density by $\Delta d = \frac{M_{n+1}}{N} \cdot \Delta n$, (where $\Delta n = n_n - n_{n+1}$, i.e., the difference between the number of molecules per unit volume of the compounds with n and n+1 carbon atoms in the hydrocarbon chain), the actual density is found to be:

$$d_{n+1} = d'_{n+1} - \Delta d = \frac{M_{n+1}}{M_n} \cdot d_n - \frac{M_{n+1}}{N} \cdot \Delta n.$$

Multiplying and dividing the last term by d_n, we get, after some rearrangement:

$$d_{n+1} = d_n \left(\frac{M_{n+1}}{M_n} - \frac{M_{n+1}}{M_n} \cdot \frac{\Delta n}{n_n} \right) = d_n \cdot \frac{M_{n+1}}{M_n} \left(1 - \frac{\Delta n}{n_n} \right). \qquad (2)$$

Table 3 gives the values of $\Delta n/n_n$ computed from Equation (2); the relative decrease in the number of molecules per unit volume as the hydrocarbon chain is lengthened by one CH_2 group. As this table indicates:

TABLE 3

Number of carbon atoms in hydrocarbon groups	$C_nH_{2n+1}X$							
	X = CH_3 (20°)	X = F (20°)	X = Cl (20°)	X = Br (20°)	X = SH (0°)	X = CN (0°)	X = $COCH_3$ (20°)	X = NO_2 (25°)
n = 1	–	–	–	–	0.254	0.256	–	0.253
2	–	–	–	0.177	0.183	0.197	0.184	0.191
3	–	–	0.154	0.153	0.157	0.161	0.155	0.160
4	–	0.136	0.137	0.135	0.135	0.138	0.139	–
5	0.118	0.123	0.120	0.118	0.119	0.122	0.121	–
6	0.108	0.111	0.106	0.105	0.106	0.108	–	–
7	0.099	–	0.097	0.096	0.095	0.098	–	–
8	0.090	–	0.091	0.087	0.087	0.089	–	–
9	0.083	–	0.082	0.084	–	0.081	–	–
10	0.076	–	0.074	–	–	0.075	–	–
11	0.070	–	0.069	–	–	–		

a) $\frac{\Delta n}{n_n}$ depends upon the number of carbon atoms in the hydrocarbon chains of the initial compounds; as this number increases, $\frac{\Delta n}{n_n}$ drops, this drop being steeper in the first few members of the homologous series than in the last ones. In other words, the larger the size of the molecule, the smaller the absolute as well as the relative decrease in the number of molecules per unit volume as the hydrocarbon chain is lengthened by one CH_2 group;

b) when the number of carbon atoms in the hydrocarbon chains remains constant, $\frac{\Delta n}{n_n}$ suffers an only negligible change as the nature of the functional group is varied (the departure from the mean value does not exceed 1-2% as a rule;

c) $\frac{\Delta n}{n_n}$ is changed (diminished) fairly little as the temperature is raised: this likewise follows from the data on $\frac{\Delta n}{n_n}$ at various temperatures for normal saturated hydrocarbons, listed in Table 4.

What has been established above enables us to shed light upon the singular-

ities of density changes in homologous series. As the number of carbon atoms in hydrocarbon chains is increased, $\frac{\Delta n}{n_n}$ approaches zero, and $\frac{M_{n+1}}{M_n}$ approaches unity. Hence, when the number of carbon atoms is infinite, d_{n+1} equals d_n, i.e., it reaches the asymptotic value of the density for the given series. Inasmuch as $\frac{M_{n+1}}{M_n}$ cannot equal unity, and $\frac{\Delta n}{n_n}$ can never equal zero, $d_{lim.}$ is merely a figure that the density of the series approaches asymptotically.

However, to judge from the nature of the changes of $\frac{M_{n+1}}{M_n}$ and $\frac{\Delta n}{n_n}$, as the hydrocarbon chains are lengthened, the limiting value of the density may be reached long before the number of carbon atoms approaches infinity; this occurs when $\frac{M_{n+1}}{M_n} - \frac{M_{n+1}}{M_n} \cdot \frac{\Delta n}{n_n}$ equals unity, i.e., when the rise in density due to an increase in the molecule mass is balanced out by the drop in density due to the decrease in the number of molecules per unit volume. As Equation (2) indicates, whenever the difference $\frac{M_{n+1}}{M_n} - \frac{M_{n+1}}{M_n} \cdot \frac{\Delta n}{n_n}$ is greater than unity, the density of the series will rise as the hydrocarbon chain is lengthened; conversely, it will fall. When it is close to unity, the density of the series will approach the limit. This explains the circumstance that homologous series of compounds with fairly low molecular weight (hydrocarbons, fluorine derivatives, etc.) are ascending series, inasmuch as their $\frac{M_{n+1}}{M_n}$ is large, whereas homologous series of compounds with comparatively high molecular weight (bromine and iodine derivatives and the like) are descending series, inasmuch as their $\frac{\Delta n}{n_n}$ is nearly the same, while their $\frac{M_{n+1}}{M_n}$ is fairly small.

TABLE 4

Number of carbon atoms	$\frac{\Delta n}{n_n}$ at			
	20°	30°	40°	50°
6	0.108	0.107	0.104	–
7	0.099	0.098	0.097	0.096
8	0.090	0.090	0.088	–
9	0.083	0.083	0.083	–
10	0.076	0.076	0.076	–
11	0.070	0.070	0.070	–

The tendency of the density to approach a limiting value in homologous series satisfactorily explains the above-mentioned nature of the changes in molar volume in these series. It follows from Equation (1) that the molar volume:

$$V = \frac{M}{d} = \frac{M(bn+1)}{d_{lim.}bn} = \frac{M}{d_{lim.}}\left(1 + \frac{1}{bn}\right),$$

is directly proportional to the molecular weight only when the value of n equals infinity; only in this case is the homologous difference of the molar volume, ΔV, a constant, $\frac{14.021}{d_{lim.}}$. As the number of carbon atoms in the hydrocarbon chains is increased, ΔV approaches ever closer to this limiting value, $\Delta V_{lim.}$. Inasmuch as $d_{lim.}$ changes from one homologous series to another, $\Delta V_{lim.}$ must also be different in different homologous series.

SUMMARY

1. A formula is put forward for calculating the density changes in homologous series of organic compounds.

2. It has been shown that a comparative decrease in the number of molecules per unit volume as the hydrocarbon chains are lengthened undergoes only a negligible change as the functional group is changed.

3. The nature of the changes of density in homologous series is explained by the opposite effects of the increase in mass and in the size of the molecule as the hydrocarbon chain is lengthened.

4. The singularities in the changes of molar volume in homologous series are due to the existence of a limiting density in these series.

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THE INTERNAL DISSOCIATION, COLOR, AND CHEMICAL ACTIVITY OF INNER COORDINATION AND CYCLIC SALTS*

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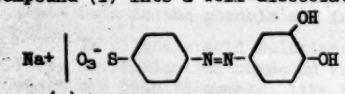
In aqueous solutions, the salts of all metals undergo electrolytic dissociation, which is nearly always rather farreaching. This holds true of the salts of organic as well as inorganic acids, including those that contain various substituents, such as m or p-hydroxybenzoic acid.

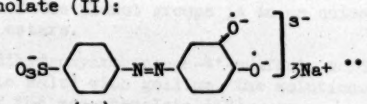
There is no reason to suppose that the nature of the bond between the carboxyl group and the metal ion must change fundamentally or significantly, provided the substituent is located so that a cyclic salt can be formed, as happens, say, in o-hydroxybenzoic acid.

On the other hand, there are various reasons for believing that various inner coordination salts and cyclic salts, in general, are characterized by an intramolecular ionic state that resembles, say, the long-recognized intramolecular ionic state of some highly colored organic compounds [5,7]. This intramolecular ionic state cannot be determined either by the minimum formula for the coordination compound or by its outer dissociation, characterized by the instability constant, but it is readily manifested in several properties of the coordination compound.

What first strikes the observer in colored compounds is their color. We shall illustrate this by means of an example. 3,4-Dihydroxyazobenzene-4'-sulfonic acid (I) forms yellow solutions in an acid or a neutral medium. When alkalinized, the color of the solution turns dark pink, owing to the conversion of compound (I) into a well-dissociated phenolate (II):



(I) Yellow solution



(II) Dark-pink solution

4-Hydroxy-3-methoxyazobenzene-4'-sulfonic acid (III) yields yellow solutions in acid or neutral media, and orange solutions (IV) in alkaline ones:

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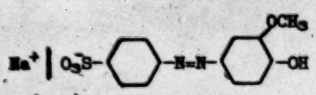
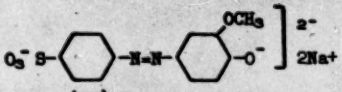
* The properties described refer to cyclic (chelate) salts in general. Inasmuch as the nature of the coordination compound is not wholly clear in many cases, the term "inner coordination" or "coordination salt" are used in this article in a collective sense, implying a cyclic salt, generally speaking.

** We denote the structural formula according to views expressed by W. Dilthey and R. Witzinger. Organic Dyes in the Light of Coordination Theory. United Scientific and Technical Press, 1936).



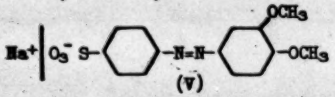
(III) Yellow solution



(IV) Orange solution

The lighter orange color of the monophenolate (IV) as against the dark-pink color of the diphenolate (II) is the result of the aggregate effect of two adjacent ionized phenol groups in compound (II).

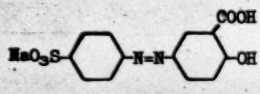
3,4-Dimethoxyazobenzene-4'-sulfonic acid (V), which does not form phenolates, is yellow in acid, neutral, and alkaline solutions.



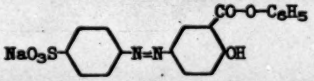
(V)

The colors of solutions of compounds (I), (III), and (V) are very similar, according to visual estimation and their absorption curves.

Hence, replacing the nonionogenically bound hydrogen in the OH groups of these compounds by a methyl group does not affect their color in the visible region. The same is true when an aryl group is substituted for the hydrogen. Solutions of compounds of the following structure are very similar in their color, as estimated visually:



and



This is a general proposition: the colors of free colored phenols are very close to those of their esters. This rule, which has been known for a long time, has again been confirmed in various instances [2].

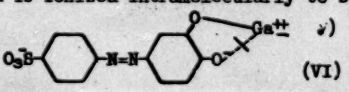
Only in esters containing heavy aryls or alkyls do we find a certain departure from the color of the phenols, but this departure is not very great as a rule.

The cited rule is important to the present paper insofar as the resemblance between the colors of phenols and those of their esters is related to the resemblance in their structure. The oxygen of the phenol groups is in an unionized state both in the phenols and in their esters.

In slightly acid solutions, 3,4-dihydroxyazobenzene-4'-sulfonic acid (I) forms a coordination compound (a chelate salt) with gallium, the solutions of which are reddish-orange, like those of the monophenolate (IV).

If both of the bonds linking the gallium atom to the oxygen in the OH group in which gallium replaces the hydrogen were fully covalent, as in the case of alkyl-substituted compounds, the color of the coordination compound ought to resemble that of the undissociated dimethoxy compound (V) or of the original compound (I), inasmuch as gallium ions have no color of their own.

Since this is not the case, it may be assumed that one Ga–O bond in this coordination compound is ionized intramolecularly to some extent, which we depict as follows:



(VI)

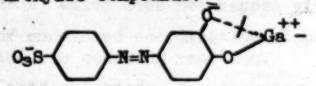
Assumptions concerning the formation of mixed gallium-sodium phenolates are highly improbable, inasmuch as alkaline phenolates are not formed in an acid medium (cf [3]). Moreover, a color reaction with gallium likewise yields the free acid (I), without any alkaline salts being formed.

The minimum composition of the gallium coordination compound, isolated in the solid state for analysis is not significant, since we are dealing with the state of the coordination compound when it is dissolved.

This hypothesis makes the close resemblance of the colors of compounds (IV) and (VI) understandable. It is also easy to see why the gallium coordination compound (VI) should have a somewhat more reddish hue. In this coordination compound, we have a OGa substituent, as it were, which produces a somewhat deeper color than the OCH_3 substituent in compound (IV).

The color of the gallium coordination compound cannot be close to the dark-pink color of compound (II), inasmuch as this would require that the bonds of both oxygen atoms be dissociated simultaneously. It is apparent that this condition can hardly be met in view of the very existence of the coordination compound in dilute solution.

The choice of the preferable structure (VI) or (VII)* for the gallium coordination compound may be founded upon the well-known fact that the color of m-hydroxyazo compounds is intensified much less upon alkalinization than is the case with ortho or para hydroxyazo compounds.**



(VII)

Assuming structure (VI) for the gallium coordination compound, analogous to structure (IV), we should expect the colors of their solutions to coincide as well as those chemical properties that require the presence of phenolic hydroxyl as a dissociated phenolate. This coincidence of properties actually exists.

The coupling of diazonium groups to the phenols, which results in the formation of azo dyes, takes place readily in an alkaline medium, all other conditions being equal. In the case of a simple phenol, the strongly dissociated phenolate (VIII) is most capable of coupling, while the weakly dissociated phenol proper (IX), which is in that state in neutral solutions, is much less subject to coupling, and, lastly, the esters of the phenols (X), which do not dissociate at all, do not couple at all.

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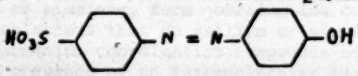
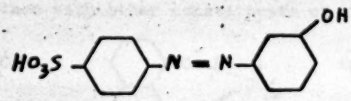
*In the light of resonance concepts, both structures may be assumed to participate in the color of the gallium coordination compound. Clearing up this problem is of no fundamental importance for the present paper.

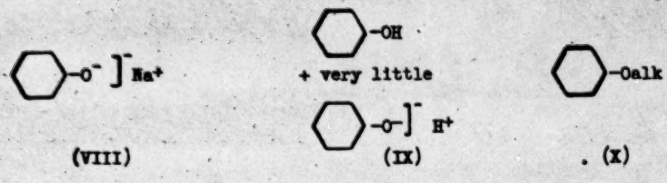
**We have found that the yellow color of alkaline solutions of p-hydroxyazobenzene-p'-sulfonic acid.



is 25 times as intense as the yellow color of the free acid or of its sodium salt, whereas in m-hydroxyazobenzene-p'-sulfonic acid



the yellow color of its alkaline solutions are only 2 to 3 times as intense as its color in a neutral or acid medium.

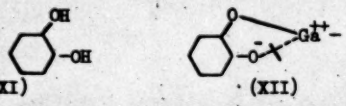


(VIII) (IX) . (X)

In a soda-alkaline medium, the phenolate (IV) is capable of combining with diazosulfanilic acid. Acidulation results in a reddish-brown solution. The gallium coordination compound (VI) can also combine with diazosulfanilic acid, giving rise to a similarly colored reddish-brown solution after phosphoric acid is added. But inasmuch as the gallium coordination compound possesses the structure required for coupling even in an acid medium, it can combine with diazosulfanilic acid in mineral-acid solutions, which does not happen with compounds (III) or (I).

The inner structure of uncolored coordination compounds may also be determined by their behavior in the azo coupling reaction.

Pyrocatechin (XI) in acid solutions, for example, is practically incapable of coupling with the same diazosulfanilic acid.

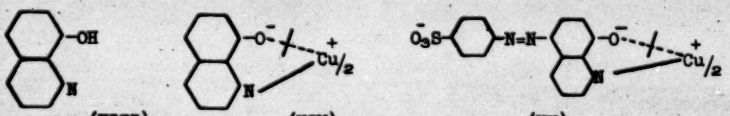


(XI) (XII)

The fact that pyrocatechin combines even in a sharply mineral-acid medium when gallium compounds are present indicates that we may assume the existence of an intramolecular ionic state (XII) in the pyrocatechin-gallium coordination compound. Coordination compounds of aluminum behave like those of gallium.

It has been previously shown that the ability of the elements to react with organic reagents of the R–OH type reflects the tendency of compounds of these elements to hydrolysis [6]. Elements whose compounds are hydrolyzed at high acidities can react with such organic reagents at high acidity.

Zirconium and germanium, whose compounds tend to hydrolyze more than do compounds of gallium or aluminum, form coordination compounds with pyrocatechin in more highly acid solutions that do gallium or aluminum. It has been found that zirconium and germanium coordination compounds of pyrocatechin are likewise characterized by the presence of an intramolecular ionic state. The zirconium coordination compound couples with diazosulfanilic acid in a sharply mineral-acid solution, whereas the germanium coordination compound couples even in a medium of some 60% sulfuric acid or in hydrochloric acid of sp. gr. 1.10. Similar phenomena take place with other constituents of coordination compounds.



(XIII) (XIV) (XV)

Thus, 8-hydroxyquinoline (XIII) practically does not combine at all with diazosulfanilic acid in a mineral-acid medium.

With copper present in the resulting copper coordination compound, the molecule of 8-hydroxyquinoline is activated so much that coupling is intensive

in a mineral-acid solution, the resulting compound settling out as a crimson-violet precipitate. As in the previous cases, the structure of the copper coordination compounds may be depicted with internal dissociation at the Cu–O bond (XIV, XV).* Inasmuch as the formation of a stable, weakly dissociated bond with amino nitrogen is quite typical for copper, dissociation along the Cu.....O bond is not unexpected. Formally, the structure (XIV) is similar to the structure, say, of the coordination compound $[Cu(NH_3)_4]SO_4$, where the Cu–N bond is not ionogenic, while the Cu.....SO_4 bond (via oxygen) is ionogenic along the Cu.....O line.

In general o-phenanthroline is unable to couple with diazonium compounds. But a ferrophenanthroline coordination compound couples vigorously with the diazoniums in sulfanilic acid or p-nitroaniline-o-sulfonic acid. Inasmuch as the o-phenanthroline coordination compound with copper does not enter into these couplings, it may be supposed that the inner structures of ferro- and cuprophenanthroline coordination compounds are different.

But in every case an intramolecular compound is more reactive than the original constituent. In contrast to copper, 8-hydroxyquinoline combines sluggishly with diazosulfanilic acid in the presence of aluminum, even after sodium acetate has been added, though this coupling proceeds rapidly under the same conditions but with no aluminum present. This means that under our experimental conditions, the O–Al bond in the aluminum coordination compound is at any rate less dissociated internally than the 8-hydroxyquinoline itself in an acetate medium. The weakly dissociated O–Al bond approaches the undissociated $-O-CH_3$ bond in 8-methoxyquinoline, which is unable to enter into phenol-type couplings.

In a moderately strong alkaline medium ($\sim$ 0.03N NaOH), 3,4-dihydroxyazobenzene-4'-sulfonic acid (I) does not form a dark-pink solution in the presence of beryllium, its color being merely orange-yellow, close to the yellow color of the free acid (I) or of its methoxy derivative. Judging from this color, we may assume that in an alkaline solution most of the molecules of the beryllium coordination compound do not exhibit any noticeable internal dissociation.

This supposition is confirmed by the chemical properties of the beryllium coordination compounds. In alkaline solutions these coordination compounds are less active chemically than the corresponding phenolates of the alkali metals.

Thus, when a solution containing pyrocatechin and p-aminosalicylic acid is alkalinized with caustic soda, the mixture instantaneously turns dark violet when shaken in the air, owing to the formation of an indophenol. When beryllium is present, such a mixture remains uncolored at first, only gradually turning pink.

Phenomena resembling those cited are observed not only in the formation of azo compounds or indophenols, but generally speaking in all cases where the properties and the reactivity of the compound depend upon its ionic state. That is why we can obtain an idea of the presence or absence and the amount of internal dissociation in the molecule of a given coordination compound by

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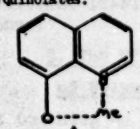
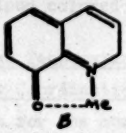
*Magnetochemical investigations led Seguin [3] to conclude that the metallic derivatives of 8-hydroxyquinoline (in the solid state) ought to possess the structure A rather than structure B, inasmuch as they are too diamagnetic to possess structure B. He gives numerical data for magnesium, zinc and cadmium 8-hydroxyquinolates.



A



B

observing the latter's reactions and comparing them with the reactions of the coordination compound constituent in the dissociated and undissociated state.

As shall be demonstrated in another paper, the magnitude of the internal dissociation depends upon the prevailing conditions (pH, temperature) and is related to the other properties of the salts of the elements and of the coordination compound constituents, which enables us to guess its order of magnitude.

Besides their original purpose – establishing our notions of the intramolecular ionic state of coordination compounds, the foregoing considerations, after further development, may well be of general interest in chemistry, inasmuch as they aid in an understanding of the relationship between the internal structure of a molecule and the properties of substances. These considerations may also be of interest in shedding light upon the mechanism of certain reactions.

Proposing to develop these considerations further in subsequent papers, we shall confine ourselves here to brief indications of the most interesting aspects.

1. Rapid Determination (By Color Reaction) Whether Uncolored Coordination Compounds Are Formed in A Solution

A (color) reaction is selected for the given coordination-compound constituent which proceeds at moderate speed under the prevailing conditions. Observation of any acceleration or retardation of the reaction due to the presence of the element in question enables one to judge whether a coordination compound has been formed under the given conditions (provided the internal dissociation of the coordination compound and that of the reagent are different under the given conditions, of course).

For example, a mixture of pyrocatechin and diazosulfanilic acid may be readily employed to demonstrate the formation by pyrocatechin of colorless coordination compounds with Al, Ga, In, Sb^{III}, Nb^{V}, Mo^{VI}, Wo^{VI}, and other elements.

The formation of soluble tartrate coordination compounds by calcium in an alkaline medium may be judged by the fact that in the presence of calcium, alkaline solutions of Rochelle salt are oxidized by permanganate more quickly than when no calcium is present. The difference in the oxidation rate is so considerable that this phenomenon may be employed as a color reaction for calcium.

A change in the reactivity of compounds after they have formed coordination compounds has been known for some time [1,8], but it seems that this is not related to a change in the internal structure of the coordination-compound constituent in the sense set forth above.

2. Approximate Estimate of the Magnitude of Intramolecular Dissociation by Comparing the Reaction Velocity of the Coordination Compound with the Reaction Velocity of Various Forms of the Coordination Compound Constituent

With colored coordination-compound constituents and elements that exhibit no chromophore action, this estimate is made by determining the ratio of various colored forms of the coordination-compound constituent that imitates the color of the coordination-compound solutions. The dissociation of the coordination-compound constituent itself in its various colored solutions is determined in the usual manner.

3. The Effect of pH and Temperature Upon the Color of Solutions of Inner Coordination Compounds

Without touching on other notions for the moment, presuming to relate differences in color of inner coordination compounds at various pH to differences in

the composition of the coordination compounds (as in [4], say), the differences in color may be attributed to the differences in the intramolecular ionic state of the coordination compound. It is easy to understand the effect of pH and temperature upon the color of solutions of coordination compounds if we remember the effect that these factors may have upon the (intramolecular) ionic state of a coordination compound.

If we stay within the confines of the stability of coordination compounds, reducing the pH increases the intramolecular dissociation. In this connection, at low values of pH the solutions of coordination compounds are colored more intensively and sometimes in a different hue than at high pH values. If the reagents are colored and the elements possess no chromophore action, the color of solutions of coordination compounds approaches the color of solutions of the alkaline phenolates, the lower the pH, the stronger being the color.

The pH and the temperature have the same effect upon the color of solutions of coordination compounds formed by colorless reagents and elements that exhibit chromophore activity. This enables us to comprehend the effect of the nature of the substituent in a phenol, and the effect of the pH and the temperature upon the color of solutions of coordination compounds of iron with the phenols.

4. Searching for New Color Reactions for Various Elements

These reactions are based upon an increase in the activity of the coordination-compound constituent. For instance, an acidulated mixture of pyrocatechin and diazosulfanilic acid turns red slowly when zirconium, niobium, wolfram, and some other elements are present, which may serve as a color reaction for these elements.

These color reactions are interesting because the may be exhibited by elements that possess no chromophore effect reacting with uncolored reagents.

5. A Change in the Concept of the Structure and Properties of Some Inner Coordination Salts

Some inner coordination compounds, such as copper 8-hydroxyquinolate, used in its gravimetric form in analysis, or ferro-o-phenanthrolin possess high enough chemical activity, which might be borne in mind in special cases.

Allowance for intramolecular dissociation might be useful in general in studying the structure of coordination compounds. We cannot fail to mention that the structure of many inner coordination compounds is often given rather arbitrarily in the chemical literature, especially in the analytical literature.

6. Catalytic Action of the Elements

The concept of the increased chemical activity of some coordination compounds in individual cases may be extended to catalytic reactions to explain the mechanism of catalysis, the effect of various factors upon catalysis, and a search for new catalytic reactions.

7. Facilitating the Performance of Some Organic Syntheses That Proceed With Difficulty

Activation of the molecule of the coordination-compound constituent enables us to perform reactions under conditions that impede the side processes and to accelerate sluggish reactions. For example, the production of azo dyes from pyrocatechin by the usual manner (in an alkaline medium) is hampered by the simultaneous oxidation of the pyrocatechin under the influence of diazonium. In the presence of salts of aluminum and other elements, pyrocatechin couples readily in an acid medium, where the diazonium is not oxidized.

In the presence of calcium salts, it is easy to secure diazo compounds (from diazosulfanilic acid, for instance) from chromotropic acid, which are hard to synthesize by ordinary methods. The production of azo compounds by coupling diazoniums with ortho phenanthroline or with quinaldic acid is effected readily in the presence of salts of bivalent iron, but does not take place at all if no iron is present.

In view of the intramolecular dissociation of coordination compounds, there should be no difficulty in finding similar instances in which synthesis is facilitated as well as means of controlling the course of reactions.

SUMMARY

Many inner coordination compounds, and cyclic salts in general, in the dissolved state are characterized by the presence of intramolecular dissociation.

In coordination compounds formed from colored reagents, the internal dissociation of the coordination compounds may be determined by the color of their solutions. The color of these solutions reflects the color of the dissociated form of the coordination-compound constituent.

The internal dissociation of colored and uncolored coordination compounds may also be discovered from their chemical properties. The properties of a bound coordination-compound substituent are determined by its ionic state in the coordination compound. In an acid medium, solutions of coordination compounds of the phenols with some metals possess the properties of solutions of the alkaline phenolates; they combine with diazonium compounds, etc.

Examples are cited of the difference in the chemical behavior of a coordination compound and of the coordination-compound constituent (for identical values of the pH).

The concepts of the intramolecular ionic state are useful for: 1) rapid determination of the formation of a coordination compound in a solution; 2) a proximate estimate of the magnitude of intramolecular dissociation; 3) an understanding and an explanation of the effect of pH and temperature upon the color of solutions of coordination compounds; 4) a search for new color reactions for various elements; 5) the development of concepts of the structure and properties of intramolecular salts; 6) explaining and finding new instances of the catalytic action of the elements; and 7) facilitating the performance of some syntheses.

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[7] A.N.Terenin. The Photochemistry of Dyes. USSR Acad. Sci. Press, Moscow-Leningrad, 1947, pp. 27, 35.

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THE EFFECT OF pH UPON THE COLOR OF SOLUTIONS OF INNER COORDINATION AND CYCLIC SALTS

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THE COLOR OF SOLUTIONS OF CYCLIC SALTS *

Inner coordination salts or, generally speaking, cyclic salts of the phenols may be regarded as phenolates, irrespective of whether they are salts of alkali or any other elements. As has been pointed out previously [12], all such phenolates exhibit no fundamental differences in many of their properties, provided these properties are compared for similar states of the phenolates. The latter condition covers an identical extent of dissociation, which is of the ordinary type in alkali phenolates and "intramolecular" in the cyclic phenolates of other elements.

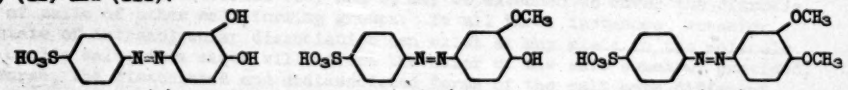
Identical dissociation of the phenolates of various elements is possible, but it occurs at dissimilar values of pH. Thus, solutions of the phenolates of the alkali metals dissociate readily in a strongly alkaline medium, the phenolates of many bivalent metals dissociating in a weakly alkaline, neutral, or weakly acid medium, while the phenolates of trivalent and quadrivalent elements usually dissociate only in a strongly acid medium.

For many polyvalent elements, this dissociation is exhibited as an intramolecular dissociation in their cyclic salts, and direct methods of demonstrating the presence of this sort of dissociation have been described earlier [12].

In colored phenols and colorless cations ** of the elements, this intramolecular dissociation is also responsible for the observed shade of color of cyclic-salt solutions.

This relationship stems from the following analogy. As we know, esterification of a colored phenol does not entail any appreciable change in its color. This rule was recently confirmed once again by a comparison of the respective absorption curves [20].

In this connection, the colors of solutions of the following compounds, (I), (II) and (III):



(I) (II) (III)

* The collective term "chelate" [is] (chela - "claw") is likewise employed to designate the cyclic - "clawlike" configuration of a salt.

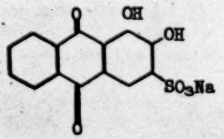
** More precisely, in cations that exhibit no chromophore activity.

are practically identical when estimated visually. The similarity of color is related to a similarity of state; neither the esters nor the phenols dissociate to any appreciable extent in acid solutions. Therefore, regarding metal phenolates as a sort of phenol esters, we may expect the colors of phenols and phenolates to be alike whenever the latter are in the same undissociated state as the phenols. On the other hand, the transition from a colored phenol to a well-dissociated phenolate usually involves a marked change and intensification of the color.* In this latter case, the change in color is due to a change in the ionic state of the molecule of the colored compound, which exerts a particularly marked effect upon the color [5].

If internal dissociation were as strongly manifested in solutions of cyclic phenolates of the heavy metals as in solutions of the alkali phenolates, the colors would be practically the same in both cases. When the intramolecular dissociation is less, the colors will lie in between the color of the phenol and the color of the alkali phenolates.

In fact, the red to orange colors of solutions of the cyclic salts of Al, Ga, Sb, In, Zr, and other elements with 3,4-dihydroxyazobenzene-4'-sulfonic acid, for example, lie between the yellow color of a solution of free phenol (I) and the crimson color of solutions of alkali phenolates, and they may be reproduced very closely by adding these two colors. The colors of solutions of cyclic salts also coincide very well with the colors of solutions of the reagent for suitable pH values, corresponding to an incomplete conversion of the reagent into the alkaline form.

Similarly, the orange, red, pink, or violet colors of solutions of the cyclic salts of various elements with alizarin S (IV)



(IV)

may be satisfactorily reproduced by adding the yellow color of the reagent in an acid medium to the violet color in an alkaline medium, or sometimes even better, by adding the yellow and pink colors in a sodium-acetate medium. At suitable values of pH, the color of solutions of alizarin S resemble the color of solutions of the latter's cyclic salts very closely.

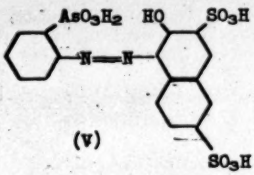
To be sure, the color resemblance cannot be absolute. But the resemblance is great enough, however, to remove any doubt concerning the general validity of the principles responsible for the color. The color of solutions of cyclic salts of an R—OH reagent is due to the ionic state of the reagent molecule, which is intermediate between the colors of the ionized and nonionized forms of the colored reagent.

This rule is a universal one, and it may be extended to cover the dissociation of salts of other salt-forming groups. In all three instances, whenever the state of intramolecular dissociation can exist at any place in the molecule of a cyclic salt, this state will affect the color of the salt somehow, provided, of course, the dissociated and undissociated forms of the salt have different colors.

The azo group may take part in salt formation and affect the color of the cyclic salts if it is suitably located in the molecule. When this is so, the colors of solutions of cyclic salts must be compared with the colors of the azo compounds in concentrated acids, where the azo group forms a salt.

*The relationship is reversed in dithiocarboxylic acids, which are of a deeper color than their salts [16].

Yellow solutions of the reagent previously described, benzene-2-arsonic acid- (1-azo-1)-2-hydroxynaphthalene-3,6-disulfonic acid (V) [7,11] ,

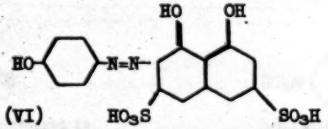


(V)

turn a raspberry red with thorium and the rare-earth elements; this cannot be attributed to the ionization of the phenolic hydroxyl alone, inasmuch as alkaline solutions of the reagent turn only a pink-orange even when heated. But solutions of the reagent in concentrated sulfuric acid are a raspberry red that is close to the color of solutions of the cyclic salts.

When the molecule of the reagent contains several substituents, there may be somewhat different colored forms at different pH values, owing to their successive ionization.

A reagent of the structure (VI)



(VI)

turned violet and pure blue at pH values that lie in between the bluish-red color in a mineral acid and the brown-orange color in ammonia. Correspondingly, solutions of the aluminum salt of this reagent are violet, while the calcium salt solution is pure blue in an ammonia medium.

In estimating the degree to which the colors of the sum of the reagent's ionic forms coincide with the colors of the cyclic salts, we must remember that the cyclic salts are not actually a simple mechanical mixture of ultimately different ionized and nonionized forms of the reagents, of course.

This may be very clearly seen in the absorption curves. For many reagents, the absorption curves of variously colored forms are fairly similar in appearance, differing principally in their locations. When the reagent is transformed from one colored form into another, what happens, in the main, is merely a shift of the curve, but not a change in its appearance. Such cases graphically illustrate the fact that the shape of the absorption curves of cyclic-salt solutions resembles that of the absorption curves of both forms of the reagent and lies between them (Fig. 1; cf also [15,16,22]). But the absorption curves of the different forms of the reagent differ sharply from the absorption curves of cyclic salt solutions (Fig. 2); it is only because of the eye's ability to add up colors that we get the physiological impression that these colors are alike.

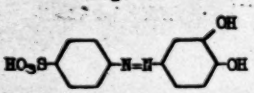
Instances of Colors That Are Not Comparable

To be sure, all the foregoing color comparisons are usable only in the simplest cases. Not always can the ionized states and their related colors that are observed in cyclic-salt solutions be reproduced in solutions of the pure reagent.

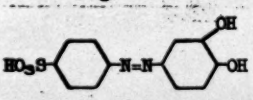
Let us discuss the case of an azo compound that contains both a NH_2 and an OH group.

Fig. 1.

Fig. 2.



1-Reagent in water, yellow; 2-reagent in NH_4OH, reddish-orange; 3-Sb^{III} salt with a pH - 4.3, orange-yellow; 4-Al salt at pH - 4.3, orange.

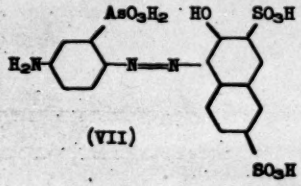


1-Reagent in water, yellow; 2-reagent in KOH, crimson; 3-Sb^{III} salt at pH - 1.6, orange-red; 4-overall color of the yellow and crimson forms of the reagent, imitating the color of the Sb salt at pH - 1.6

As regards the solution of the reagent in a neutral medium, the NH_2 group affects its color during a transition into the acid region, while the OH group controls the transition into the alkaline region. It is evident that the aggregate effect of these substituents is not compatible in solutions of the pure reagent and of its alkaline phenolates.

But in the cyclic salts of some elements, which possess the structure of ionized phenolates in an acid medium, the effects of the OH and NH_2 groups upon color may be additive.

This occurs in the cyclic salts of the previously described reagent (VII) [8]:



(VII)

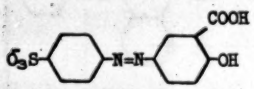
which turn pink in concentrated sulfuric acid, yellow in a sharply acid medium, pink in a slightly acid medium, and brownish-orange in a neutral or alkaline medium.

Thorium reacts in an acid medium, turning violet, as previously stated [8]. The rare earths can yield a color reaction only in a neutral medium, turning

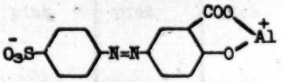
brownish pink.

Colors that are not comparable are often encountered in the cyclic salts of boron, whose cation is often hydrolyzed in concentrated acids, where salt formation is caused by the azo group or the oxygen atoms of the anthraquinone group. Benzene-2-arsonic acid- (1-azo-2)-1,8-dihydroxynaphthalene-3,6-disulfonic acid reacts with boron in sulfuric acid, turning green-blue, whereas the color of the reagent itself is merely blue-violet in sulfuric acid and pink in water and alkalies.

A special type of incomparability often encountered involves a difference in the intensity of the colors, rather than in their hues, which is due to the presence of a more prominent ionic state in the cyclic salt than in the solutions of the pure reagent. Thus, yellow solutions of 4-hydroxy-3-carboxyazobenzene-4'-sulfonic acid (VIII)



(VIII)



(IX)

is 3.5 times less intense at a pH = 4.5 than an equimolecular concentration of its Al salt in solution at the same pH (IX). When the pH of the solution of the cyclic salt is increased considerably, the free valency bond of the aluminum in the latter is hydrolyzed, its ionic state vanishes, resulting in the disappearance of the effect of this state upon the color; this causes the color to grow paler.

Similarly, in solutions of ferritartrate coordination compounds, the yellow color is twice as intense at a pH of 5.5 as it is at a pH of 9. This interesting influence of the pH upon the intensity of the color of cyclic salts will be discussed in greater detail in a special report.

In general, colors that are not comparable are encountered in reagents that contain several different salt-forming groups, whose salt formation affects the color and takes place at different pH values.

In such systems, the complex internal effect upon the color of the cyclic salts may strikingly reflect the nature of the element entering into the salt as well as the introduction of various substituents into the reagent. All this makes this kind of compound an interesting reagent for color reactions of various elements. Some examples of such color reactions are listed in Table 1.

The Effect of the pH upon the Color of Cyclic-Salt Solutions

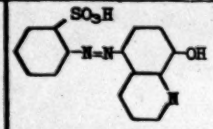
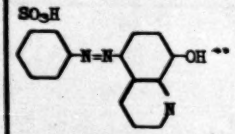
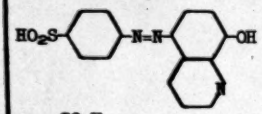
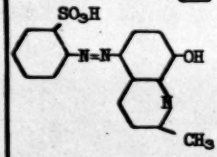
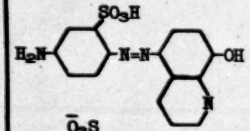
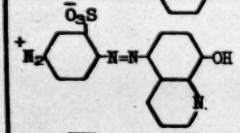
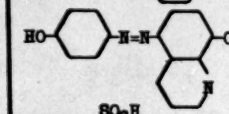
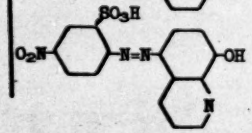
After our discussion of the foregoing data, explaining the effect of the pH upon the color of solutions of intramolecular salts and cyclic salts, in general, presents no difficulty. This effect consists of a change in the amount of intramolecular dissociation, the significance of which for color is obvious from what has been set forth above.

Organic reagents of the R–OH type do not react at all with metal cations in solutions that are excessively acid. As the pH rises, about to the value at which solutions of simple salts of the given element begin to hydrolyze, i.e., at which even a single undissociated Me–O bond can be formed, the reaction sets in [10].

For example, in 3,4-dihydroxyazobenzene-4'-sulfonic acid (I), which yields yellow solutions, a cyclic salt of the following structure is formed:

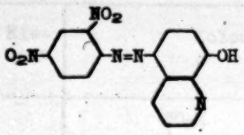
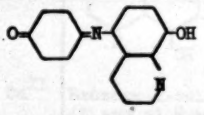
TABLE 1

Color Reactions of Copper, Silver, Mercury, and Cobalt with Azo Derivatives of 8-Hydroxyquinoline

No	Compound	Colors				
		One reagent	Cu^{II}	Ag	Hg^{II}	Co
1		Yellow	Blue	Crimson	Greenish-crimson	Bluish-crimson
2		Orange-yellow	Brownish-pink	Brownish-pink	Brownish-pink	Pink
3		Yellow	Red-brown	Blue-crimson	Red-brown	Bluish-crimson
4		Yellow	Brownish-pink	Pink	Pink	Pink
5		Yellow	Dirty green	Red-violet, then violet-black	Blue-violet	Blackish-lilac
6		Greenish-yellow	Brownish-light-blue	Dirty olive	Greenish-light blue	Light blue
7		Brownish-yellow	Brownish-yellow	Brown-red	Orange	Yellow-brownish
8		Brownish	Pink	Brownish-violet	Bluish-pink	Pink

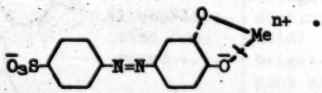
See footnotes, next page.

TABLE 1 (Continued)

No.	Compound	Colors				
		One reagent	Cu^{II}	Ag	Hg^{II}	Co
9		Greenish-yellow	Brown	Brownish-violet	Red-violet	Violet
10	Indophenol 	Reddish-yellow	Grass-green	Blue-violet, turning to gray-black	Violet-gray	Blue-violet

The colors depend markedly upon the pH. The indicated colors (solutions + precipitates) apply to the pH that is best suited for each case.

This compound was investigated as an analytical reagent, but under conditions that were wholly unsuited to this purpose: in approximately 10% hydrochloric or nitric acid, as a result of which its color reactions remained unnoticed [14] (cf [10]).



The other valency bonds of the ion are as yet nonionogenic. The valency bond that closes the ring is also partially ionogenic. That is why intramolecular dissociation occurs in this cyclic salt, and the color of the cyclic-salt solution that corresponds to its magnitude approaches the color of solutions of well-dissociated alkaline phenolates. In the present instance, this color will be pink or red.

As the pH is raised still higher, the intramolecular dissociation of the cyclic salt decreases, and as a result, the color of the latter's solutions pass through an orange tone and approach more and more closely to yellow, which is typical of the undissociated form of the original reagent.

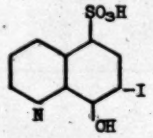
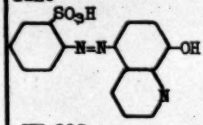
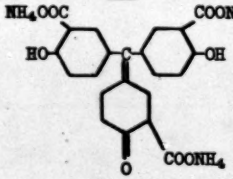
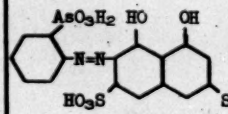
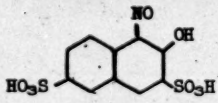
Obviously, the cyclic salts of various elements may exhibit different colors at the same value of pH. Thus, with the above reagent, a solution of a salt of trivalent antimony is yellow at pH = 6, whereas the aluminum salt is red. This is quite understandable, since we know that the salts of trivalent antimony are hydrolyzed at a lower pH than salts of aluminum.

This simple relationship is a general rule: as the pH is raised, the color of solutions of already existing cyclic salts changes so as to make the shade approach the color of the undissociated form of the colored reagent. In general, this rule applies to salts of elements that exhibit no chromophore action (Fe, Co,

The bond that is intramolecularly dissociated is denoted by the dashed line and the signs of the charges are attached to the atoms involved.
This structure is to be regarded as simply the structure of the predominating content. It is possible that other structures may be present.

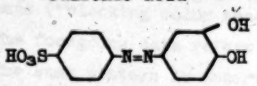
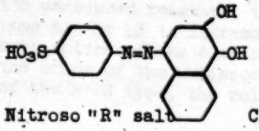
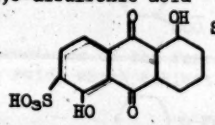
TABLE 2

Effect of pH Upon the Color of Solutions of Intramolecular and Cyclic Salts.
A. Colored Reagents (Coordination-Compound Constituents) of the R-OH Type.

No.	Element	Colored reagent	Solution color: Acid medium	Solution color: Urotropin or sodium acetate added	Solution color: Ammonia added
1	Fe^{III}	 "Ferron" Fe^{III} coordination compound. One reagent.....	Dark green Pale yellow	Dirty brown Yellow	Orange Barely yellowish
2	Cu^{II}	Benzene-2-sulfonic acid-(1-azo-5)-8-hydroxyquinoline  Cu^{II} coordination compound. One reagent.....	Crimson, turning to blue precipitate Yellow	Yellow Yellow	Yellow precip. Yellow
3	Al	 "Aluminion" Al coordination compound ..... One reagent.	(slightly acetic acid) bright-pink precipitate Barely pinkish	Pale brownish* Pale brownish	
4	Ti^{IV}	Benzene-2-arsonic acid-(1-azo-2)-1,8-dihydroxynaphthalene-3,6-disulfonic acid  Ti^{IV} coordination compound..... One reagent	Red-violet Red-pink	Red-violet Pink	Dark pink Dark pink
5	Zr	 Nitroso-"R" salt $Zr^{\cdots}$ coordination compound One reagent..	(Strongly hydrochloric) Orange Light-yellow	Yellow Yellow	

*A colored solution results when the reagent is present in great excess; when the excess is not so great, a suspension is formed.

Table 2 (continued)

No.	Element	Colored reagent		Solution color		
				Acid medium	Urotropin or sodium acetate added	Ammonia added
6	Sb^{III}	1,2-Dihydroxyazobenzene-4'-sulfonic acid 	Sb^{III} salt	Orange-red	Yellow	
			One reagent....	Yellow	Yellow	
7	Sb^{III}	1,2-Dihydroxynaphthalene-(4-azo-1)-benzene-4-sulfonic acid 	Sb^{III} salt	Violet	Orange	
			One reagent.....	Orange	Orange	
8	Co^{III}	Nitroso "R" salt	Co^{III} coordination compound.....	Red-brown-orange	Red-brown-orange	Yellow-brown
			One reagent.	Yellow	Yellow	Brownish-olive
				Concentrated sulfuric acid		Concentrated sulfuric acid, diluted with equal volume of water
9	B	1,5-Dihydroxyanthraquinone-2,6-disulfonic acid 	B coordination compound.....	Pink		Yellow
			One reagent.....	Yellow		Yellow
10	Ge^{IV}	1,5-Dihydroxyanthraquinone-2,6-disulfonic acid	Ge^{IV} coordination compound...	Pink		Yellow
			One reagent	Yellow		Yellow

Cu, etc.), but it is sometimes applicable without this restriction (Table 2).

Cases are conceivable in which the colors of solutions of the cyclic salt and the reagent are practically identical at a given pH. We may frequently judge whether the cyclic salt is at all present in such solutions by the presence of the element in solution – when no soluble reagent is present, the element settles

out as a hydroxide. This is often observed for antimony and other elements, whose salts hydrolyze readily.

If a cyclic salt that does not exhibit intramolecular dissociation is not decomposed in alkaline solutions, its color corresponds to that of acid solutions of the reagent when the reagent used is of the R–OH type. This color is usually not as deep as that of alkaline solutions of the reagent. Formation of the cyclic salt "blocks" the grouping of the reagent and does not allow it to enter the ionized state ("blocking color reaction").

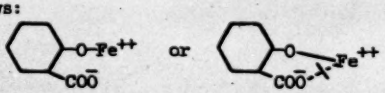
The foregoing data refers to colored reagents and uncolored metal cations.

The same pattern is observed in the case of the cyclic salts that are formed by uncolored reagents and elements that exhibit chromophore activity. The latter include the elements whose compounds are either colored or absorbent in the near ultraviolet (Fe, Cu, Cr, Co, etc.).*

With uncolored reagents, the intramolecular dissociation of the cyclic salts again drops as the pH is increased. But, inasmuch as the color depends upon the chromophore action of the element in this instance, the hue of the color will approach the color of the undissociated form of the element's compound. With reagents of the R–OH type, the color of the element's hydroxide is a limit of this sort.

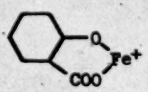
That is why the color of the solutions of all such cyclic salts approaches the color of the element's hydroxides when the medium is sufficiently alkaline, provided no decomposition or change has already occurred. For instance, the color of cyclic salts of trivalent iron approaches the brown-yellow color of ferric hydroxide, chromium salts turn green, and titanium salts are decolorized, since neither the reagent nor the hydroxide of the element is colored.

In acid solutions the ferrisalicylate coordination compound is violet, while it is brown in neutral media. In the light of the structural comments set forth above, the violet (not the brown!) coordination compound in the solution may be represented as follows:



like the structures of the ferric coordination compounds of phenol or of phenol-o-sulfonic acid, which exhibit the same violet color:

but not as



(as is sometimes done in the literature [1]).

Opinions Expressed in the Literature on the Variation of the Color of Cyclic-Salt Solutions with the pH

The literature contains many references to the variation of the color of cyclic-salt solutions with the pH. Ignoring the older papers, we might note that the varying color is said to be due to differing composition of the coordination compounds (chelate salts [4]), according to the latest notions (1947).

*The effect of the chromophore activity of elements upon the color of coordination salts and of cyclic salts in general will be discussed in a separate paper.

For instance, A.K.Babko gives the following relationship for cyclic ferric salts with pyrocatechin (R group of the pyrocatechin) [2]:

Medium	Color	Composition
Acid	Green	FeR^+
Neutral	Violet	FeR_2^-
Alkaline	Red	FeR_3^{---}

Similar figures are given for the cyclic salts of the ferrisalicylates [1], the cuprisalicylates [3], etc.

Similar results are cited for the ferric salts of pyrocatechindisulfonic acid by Joe and Jones [21], who also note that the mechanism governing the color shift is not definitely established. To judge by the structure they cite (cf the original), these authors relate color to the extent of coordination of the iron: 4 - blue; 5 - violet; and 6 - red.* Similar views are expressed in many other papers.

In discussing these considerations, without touching upon the composition of the salt in detail, the color of the ferric salts of pyrocatechin or of pyrocatechindisulfonic acid must change when the pH is changed, owing to a change in the ionic state of the iron atom and in the ionic state of the oxygen atoms in the phenolic hydroxyl groups. The number of the latter rises at first during a transition from acid to alkaline solutions and then drops, owing to the step-by-step-formation and decomposition of complex coordination compounds.

After the ionic state of the oxygen atoms in the phenolic hydroxyl groups has disappeared as the result of the partial decomposition of the complex coordination groups, the color of the remaining soluble cyclic ferric salts ought to be close to that of ferric hydroxide, according to our hypothesis.

These requirements of the hypothesis have been fully confirmed by experiment.

When a concentrated solution of KOH is added to solutions of ferric coordination compounds of pyrocatechin or pyrocatechindisulfonic acid, the red color of the slightly alkaline solutions changes to orange and then to an intense yellow, no formula having been suggested for these compounds in the literature as yet. When the yellow solutions are heated (and even in the cold in the case of the coordination compounds of pyrocatechindisulfonic acid), the addition of solid KOH results in a marked weakening of the color intensity. The resulting intensity of the color of the yellow solutions in this state is close to that of the color of a fine suspension of ferric hydroxide of equivalent concentration. When the solution is diluted with water, the color reverses.

The existence of a slightly colored soluble state is readily proved for ferric cyclic salts of sulfosalicylates as well. Here, too, the fact that such a state exists is hard to bring into agreement with the views expressed in the literature [1].

When a dilute solution of caustic soda is carefully added to the intensely yellow ammoniacal solution of a ferrisalicylate cyclic salt, we note that the intensity of the color begins to pale, finally approaching a color that is close to the color of a ferric-hydroxide suspension of equivalent concentration. When more caustic soda is added in excess to the resulting transparent solution, the color does not undergo any further noticeable change, but the solution turns cloudy, as the result of decomposition of the cyclic salt and precipitation of the ferric hydroxide.

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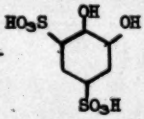
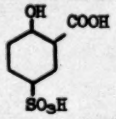
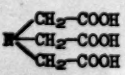
*In a later magnetochemical investigation of these coordination compounds it was found that the bonds of the iron atoms are essentially ionic. [10].

TABLE 3

Effect of pH upon the Color of Solutions of Inner Coordination and Cyclic Salts

B. Uncolored Reagents of the R — OH Type

No.	Element	Uncolored reagent	Solution color: (slightly) Acid medium	Solution color: Urotropin or sodium acetate added	Solution color: Borax, ammonia, or caustic soda added	Color of the element's hydroxide
1	Fe^{III}	a. Pyrocatechindisulfonic acid 	Green-blue	Violet	Red; orange and yellow in an excess of NaOH	Brownish-yellow
2		b. Sulfosalicylic acid 	Brownish-pink	Intense brown	Yellow, less intense	Brownish-yellow
3		c. p-Aminophenoldisulfonic acid	Bluish crimson	Brown	(Decomposes)	Brownish-yellow
4	Cu^{II}	a. Sulfosalicylic acid		Yellow green	Bluish-green	Light blue
5	Ti^{IV}	a. Pyrocatechin	Brown precipitate	Intense orange	Nearly colorless solution (barely yellowish)	White
6		b. Pyrocatechindisulfonic acid	Brownish-orange	Intense brownish-orange	Ditto	White
7		c. Gallic acid	Brown	Intense brown-orange	Yellowish * (much NaOH)	White
8		d. Sulfosalicylic acid	Light yellow	Intense yellow	Pale yellowish	White
9	U^{VI}	a. Sulfosalicylic acid		Intense orange	Yellow	Yellow
10	Cr^{III}	a. Chromium sulfate (green)	Green-light blue	Yellow-green		Green, yellowish tinge
11		b. Nitrilotriacetic acid** 	Bright violet	Bright violet	Bright green	Green, yellowish tinge

* The reagent itself turns brown.

** The composition of this coordination compound was not investigated. The coordination compound is readily formed by heating a salt of trivalent chromium with nitrilotriacetic acid.

According to the literature, changes in the color of pure inorganic coordination compounds ("inorganic indicators") as the pH is varied are due to a change in the composition of the coordination groups. For example, the ultraviolet absorption spectrum changes in the reaction $[Pt{\cdot}6NH_3]Cl_4 + NaOH = [Pt{\cdot}5NH_3{\cdot}NH_2]Cl_3 + +NaCl + H_2O$ [17].

The red-violet aqueous solutions of chromitetraquodipyridine chloride, $[CrPy_2(H_2O)_4]Cl_2$, turn into the whitish gray-green, slightly soluble coordination compound $[CrPy_2(OH)_2(H_2O)_2]Cl$ when acted upon by ammonia or pyridine (P. Pfeiffer, 1906 [6]. The colors and the reversibility of the color transformations indicate that this compound resembles Compound No. 11 in Table 3, with nitrilotriacetic acid. The author's observations indicate that the considerations set forth above generalize and explain a large number of facts. Nevertheless, the author is far from believing that the cited concepts are completely developed.

What we need is a quantitative investigation of these phenomena by special methods, inasmuch as the ordinary analytical determination of the gross composition of the compounds, which are isolated in solid form for this purpose, is not always suitable.

In some form or other, the cited views, which essentially deal with the color of the stage of the ionic nature of the bonds, may be applied to noncyclic coordination compounds and "simple salts" as well. These notions agree with the resonance concepts that have been so vigorously developed of late.

In some cases, the hypothesis may, the author believes, be useful in its present form. The hypothesis satisfactorily explains the effect of temperature upon the color of cyclic-salt solutions, as will be described in detail in another communication.

These considerations are also of use for understanding the internal mechanism of color analytical reactions, which interest the author very much, especially reactions with colored organic reagents. The views that have gained wide acceptance at the present time, which link color reactions to the so-called characteristic (" specific") atomic groupings, are obviously inadequate as an explanation of the internal mechanism of color reactions.

SUMMARY

The color of solutions of inner coordination salts and of cyclic salts in general, formed with colored reagents, is due chiefly to the state of their intramolecular dissociation [12].

In many instances, the colors of solutions of the cyclic salts of various elements are close to the colors of solutions of the original reagents if the pH values are suitable; they may be reproduced by adding the colors of solutions of the ionized and nonionized forms of the reagent. The colors of the ionized forms (phenolates, azo salts) are observed when the reagents are dissolved in media with different pH, as well as in concentrated sulfuric acid.

In some cyclic salts, the effect of several atomic groups upon the color may all coincide, though their effect is not additive in solutions of the pure reagent. Such colors cannot be observed in solutions of the pure reagent, nor can they be reproduced by adding the colors of its different forms.

The color of solutions of the cyclic salts formed by elements exhibiting chromophore activity and uncolored reagents approaches the color of the elements' hydroxides as the pH increases. This is due to the diminution of the intramolecular dissociation of the cyclic salts and a probable simplification of their composition, resulting in partial decomposition of more complex coordination compounds.

With colored reagents, the color approaches the color of the non-ionized form of the reagent as the pH is increased.

In accordance with the requirements of this hypothesis, we have discovered bright-yellow and pale-yellowish cyclic salts of iron with pyrocatechin and pyrocatechindisulfonic acid, which are not described in the literature. The existence of these salts is hard to reconcile with the opinions set forth in the modern literature on the link between the composition and the color of coordination compounds.

The views set forth are of interest in explaining the mechanism of analytical color reactions with some organic reagents.

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*See CB translation previous article.

THE EFFECT OF CONTINUOUS RENEWAL OF THE CATHODIC MERCURY UPON THE PROCESS OF ELECTROLYTIC REDUCTION OF ORGANIC COMPOUNDS. II

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The researches of Wilson [1,2] have demonstrated that electrolytic reduction effected in the usual manner with a mercury cathode is fully analogous to reduction effected with a sodium amalgam. His investigations led him to conclude that mercury as a cathode material exerts no catalytic effect upon the process of electrolytic reduction. According to Wilson, only cathodes made of porous nickel and platinized platinum exhibit such an effect.

In our first report* we showed that when the cathode mercury was rapidly renewed during the reduction of aconitic acid or quinoline and its derivatives, the rate of reduction is greatly increased, while compounds are produced that are not secured by ordinary reduction methods. An explanation based on recognition of the catalytic action of a renewed mercury cathode was offered for this phenomenon.

Moreover, we have noticed another effect of renewing the cathode mercury upon the reduction process. These latter cases are the subject of the present report.

1. Diminishing the Rate of Electrolytic Reduction During Continuous Renewal of the Cathode Mercury

In contrast to the reduction of aconitic acid or quinoline and its derivatives, the renewal of cathode mercury has a diametrically opposite effect in the reduction of naphthalene and anthracene. As has been discovered in the present investigation, when naphthalene and anthracene are reduced electrolytically with a mercury cathode in an alkaline medium, they yield the same products as when reduced by sodium amalgam [3,4], namely: dihydronaphthalene and dihydroanthracene. In both cases electrolytic reduction at the cathode with stationary mercury is found to closely resemble reduction with sodium amalgam. But in these cases, renewing the cathode mercury produces an unexpected result: the reduction process slackens, stopping entirely when the flow of mercury is fast enough – with a jet cathode, as is shown in the subjoined tabulation of the results of one series of experiments (Table 1).

The reduction of naphthalene and anthracene at an unrenewed mercury cathode in an alkaline medium is essentially reduction at a cathode consisting of an amalgam. The complete loss of the amalgam when the cathode mercury is renewed rapidly results in complete stoppage of the hydrogenation of the naphthalene and the

*Jour. Gen. Chem. 18. 1237 (1948).

anthracene. Their electrolytic reduction does not take place at all at the real mercury electrode (in an alkaline medium with rapidly renewed mercury).

Nor are naphthalene and anthracene electrolytically reduced in an acid medium. Despite numerous endeavors, we were unable to secure even traces of hydrogenation products of either one by reduction in an acid medium.

TABLE 1

Test condition	Yield of dihydronaphthalene, %	Yield of dihydroanthracene, %
Stationary mercury.....	35.0	67.3
Slowly renewed mercury (0.15 kg/min).....	4.6	49.5
Rapidly renewed mercury (0.5 kg/min)..	3.1	11.8
Very rapidly renewed mercury (1 kg/min)	0.0	0.0

2. Renewing the Cathode Mercury Has No Effect Upon the Reduction Process

Wilson found [2] that the electrolytic reduction of sorbic acid at a mercury cathode is not at all different from its reduction by sodium amalgam.

Sorbic acid, $CH_3-CH=CH-CH=CH-COOH$, yields caproic acid, $CH_3-CH_2-CH_2-CH_2-CH_2-COOH$, upon ultimate reduction; when its reduction is incomplete, three unsaturated $\Delta\alpha$-, $\Delta\beta$-, and $\Delta\gamma$-dihydrosorbic acids:

$$CH_3-CH_2-CH_2-CH=CH-COOH,$$

$$CH_3-CH_2-CH=CH-CH_2-COOH,$$

$$CH_3-CH=CH-CH_2-CH_2-COOH.$$

Wislon showed that when sorbic acid is reduced at platinum and nickel cathodes (which he includes among the cathodes that exhibit catalytic action), much of the sorbic acid undergoes complete reduction, as much as 62.8% of caproic acid being produced; a fairly large amount of the products of incomplete reduction – the $\Delta\alpha$-, $\Delta\beta$-, and $\Delta\gamma$-dihydrosorbic acids – is also secured, the $\Delta\alpha$-dihydrosorbic acid yield being fairly considerable (18% and higher).

When reduced at cathodes that exhibit no catalytic action (among which Wilson classes mercury), sorbic acid yields no product of complete reduction at all – caproic acid, and of the unsaturated acids only a mixture of the $\Delta\beta$- and $\Delta\gamma$-acids is formed.

As Wilson sees it, this difference in the reduction products is due to the absence of any catalytic action of the cathode. In this case the reduction process takes place solely as the result of the cathode potential.

To ascertain the part played by the mercury cathode in the reduction of sorbic acid, we ran reduction experiments with a mercury cathode, at various rates of mercury renewal. In complete agreement with Wilson's investigations, we were unable to detect as much as a trace of caproic acid when a mercury cathode was employed – whether the mercury was stationary or was renewed rapidly (jet cathode). In every case all we secured were the unsaturated acids – $\Delta\alpha$-, $\Delta\beta$-, and $\Delta\gamma$-dihydrosorbic acids. The percentage composition of the resulting acid mixture was hardly changed by renewing the cathode mercury, as shown in Table 2.

The slight difference in the output of the $\Delta\alpha$-acid is of no importance; the yields of the $\Delta\beta$- and $\Delta\gamma$-acids were nearly identical in both instances.

These results justify our concluding that a mercury cathode exerts no

catalytic action in the reduction of sorbic acid. What distinguishes sorbic acid is that it is readily reduced in the manner indicated (predominantly the formation of Δβ- and Δγ-dihydrosorbic acids) at a given cathode potential; there is no need for a catalyst in this case. That is why sorbic acid is reduced with identical results by amalgams of equivalent composition (sodium, ammonium), Devarda's alloy, or electrolytically at the following cathodes: mercury, cadmium, copper, tin, and zinc (according to Wilson). Nor does the medium – alkaline or acid – introduce any significant change into the reaction. For this very reason, the continuous renewal of the cathode mercury has no effect upon the reduction of sorbic acid, as proved by the present investigation.

TABLE 2

Mercury at the cathode	Yield of reduction products, % (mean of two tests)		
	Dihydrosorbic acid		Caproic acid
	Δα	Δβ and Δγ	
Stationary	4.4	50.9	0.0
Renewed	5.9	50.7	0.0

All the data cited above indicates that there are three possible cases of the variation of the electroreducing process with the renewal of the cathode mercury.

Case 1 (aconitic acid, quinoline and its derivatives) is characterized by the positive effect of renewing the cathode mercury upon the reducing process. The output of reduction products increases as the rate at which the cathode mercury is renewed is increased. These are obviously catalytic reactions, and in these reactions mercury is a good catalyst. It is advisable to employ a renewable mercury cathode in such reactions.

Case 2 (naphthalene, anthracene) is characterized by the negative effect of renewing the cathode mercury upon the reduction process. The output of reduction products decreases as the rate at which the cathode mercury is renewed is increased, dropping to zero. In this case, reduction at a cathode of stationary mercury is due to the action of the resulting amalgam of the alkali metal.

In these cases a renewable mercury cathode may be usefully employed in an alkaline medium to slow down the reduction process when electrolysis is performed without a diaphragm. This effect of renewing the cathode mercury explains the production of dihydronaphthalenes in the electrolysis of phthalic acid [5]. The use of rapidly renewed cathode mercury in these cases may eliminate the reduction process completely, while performing electrolysis without a diaphragm enables one to have only oxidative processes take place. This method is suitable for the electrolytic oxidation of phthalic acid, for instance.

Case 3 (sorbic acid) is characterized by the absence of any noticeable effect of renewing the cathode mercury upon the reducing process. The output of reduction products is unaffected by an increase in the rate at which the cathode mercury is renewed. This reaction takes place readily without the employment of catalysts; all we need here is the suitable cathode potential. In these reactions, a mercury cathode exhibits no advantages. (The concepts advanced by Wilson and referred to above are applicable only to these reactions.)

Certain singularities are noticed in each case in an acid medium.

In Case 1, the reduction process is similar to its course in an alkaline medium, provided the catalytic action of the mercury persists in the acid medium, and the prevailing conditions do not interfere. In Case 2, no reduction is to be expected in an acid medium, as has been observed to be the case with naphthalene and anthracene. In Case 3, changing the medium for the reaction should not have any appreciable effect upon the reduction process (provided no special singularities are present), as is found to be the case with sorbic acid.

TABLE 3

Test conditions	Medium			
	Alkaline		Acid	
	Yield, %		Yield, %	
	Hydrobenzoic acids	Benzyl alcohol	Hydrobenzoic acid	Benzyl alcohol
Stationary mercury.....	76.0	8.0	0.0	25.1
Rapidly renewed mercury	0.0	0.0	0.0	24.9

TABLE 4

Test conditions	Temperature	
	10°	25°
	Glyoxylic acid, yield, %	
Stationary mercury	20	26.9
Rapidly renewed mercury	30	27.3
Difference of	10	0.4

In some instances, changing the medium in which the reaction takes place may result in a significant change in the effect of renewing the cathode mercury upon the reduction process. For example, the following change in the product yield as a function of the reaction medium is observed in the reduction of benzoic acid (Table 3).

In an alkaline medium, hydrobenzoic acids and benzyl alcohol are formed. As the table (Table 3) shows, the effect of renewing the cathode mercury upon their formation comes under Case 2, as in the reduction of naphthalene and anthracene (the output of reduction products dropping to zero when the mercury is renewed rapidly). In an acid medium, the ring is not hydrogenated at all, only benzyl alcohol being formed, and renewing the mercury has no effect upon the reduction process, which corresponds to Case 3, as in the reduction of sorbic acid.

When the temperature is raised, the effect of renewing the cathode mercury (Case 1) is obliterated. We observed this marked effect of raising the temperature in our reduction of oxalic acid to glyoxylic acid, as indicated in the attached summary of the results of one series of tests, (Table 4).

EXPERIMENTAL

1. The Electrolytic Reduction of Naphthalene

The naphthalene solution used in electrolysis was prepared as follows. 2 g of naphthalene, purified by sublimation, was dissolved in 90 ml of ethyl alcohol; just before electrolysis 10 ml of an aqueous solution containing 4.5 g of caustic potash was added to the first solution. The anolyte consisted of a 10% solution of caustic potash.

In each instance 1.5 g of naphthalene was reduced at a cone-shaped cathode, with a current density of 38.5 amps per sq dm and a voltage of 12 volts. Electrolysis lasted 1 hour and 30 minutes.

The temperature was maintained at 40°. When stationary mercury was used, the electrolyte was diluted with three times its own volume of water after electrolysis was completed and then extracted with ether until all the products it contained had been extracted. The ether was driven off after the ethereal solution has been desiccated. Driving off the ether left a residue in the form of a thick oily liquid.

Part of the resulting product was subjected to bromination to convert the dihydronaphthalene into the dibromide. Recrystallization of the reaction product from alcohol yielded colorless crystals with a m.p. of 73-74°. All the physical and chemical properties of the resulting product are identical with those of

the dihydrobromide produced by brominating the dihydronaphthalene prepared by reducing naphthalene with sodium amalgam [3].

The rest of the product was treated with an alcoholic solution of picric acid. A fine yellow crystalline precipitate settled out upon standing. The product was recrystallized from alcohol; m.p. 148-149°. A test sample mixed with the naphthalene picrate prepared from naphthalene indicated no depression. It was thus proved that the oily product we had secured was a mixture of dihydronaphthalene and unchanged naphthalene.

We then reduced naphthalene with stationary mercury and with mercury that flowed slowly, rapidly, and very rapidly. A set of 10 15-g samples of naphthalene was reduced in each series. The electrolytes of all the ten tests in a set were combined, diluted with three times their own volume of water, and extracted with chloroform until all the dihydronaphthalene and the residual naphthalene had been extracted. The amount of dihydronaphthalene in the resulting chloroform solution was determined by bromination after the solution had been desiccated [3]. The results are given in Table 5.

TABLE 5

Cathode Mercury	Amount of mercury passing through the apparatus per min. (in kg)	Bromine used in bromination g	Dihydronaphthalene corresponding to the amount of bromine used g	%
Stationary.....	0.0	6.90	5.59	35.0
Moving slowly.....	0.15	0.91	0.74	4.6
Moving rapidly.....	0.5	0.62	0.50	3.1
Moving very rapidly..	1.0	0.0	0.0	0.0

We were unable to reduce naphthalene in an acid medium, despite repeated endavors.

2. The Electrolytic Reduction of Anthracene

1 gram of anthracene, purified by recrystallization from alcohol, with a m.p. of 216°, was reduced in each test. This quantity of anthracene was dissolved in 100 ml of 95% ethyl alcohol, which contained 5 g of caustic potash in solution. A saturated solution of caustic potash in 95% alcohol served as the anolyte. The cathode was made of mercury, and the anode of platinum.

Electrolysis was effected with stationary mercury at a current density of 5.3 amp per sq. dm. and a voltage of 44-45 volts. The temperature rose to 55° toward the end of electrolysis. Electrolysis lasted 45 minutes.

The catholytes of three test runs were combined. After the cloudy solution had cooled, a copious precipitate settled on the bottom of the vessel; it was filtered out. This precipitate proved to be unchanged anthracene (0.70 g). Then the transparent filtrate was brought to a boil, and water was added until it turned cloudy. Upon cooling, 1.50 g of a precipitate with a m.p. of 103-105° settled out. Another 0.54 g of a precipitate with a m.p. of 104-105° was recovered from the filtrate by the same method. The last two precipitates were combined and dissolved in alcohol. The resulting solution was brought to a boil and diluted with water until it turned cloudy. Upon cooling we secured a precipitate with a m.p. of 105°. A test sample, mixed with dihydroanthracene prepared by the Wieland method [4] exhibited no depression. All the other physical and chemical properties of this product were wholly identical with those of dihydroanthracene prepared by reducing anthracene with sodium amalgam.

We then reduced anthracene with stationary mercury and with slowly, rapidly, and very rapidly renewed mercury. In each case, a set of 10 samples, with 10 g of anthracene in each, was reduced. The electrolytes of each set of ten tests were combined, and the dihydroanthracene isolated from them. The test results are listed in Table 6.

We were unable to effect the reduction of anthracene in an acid medium, despite repeated efforts to do so.

TABLE 6

Cathode mercury	Amt. of mercury passing through the apparatus per minute	Yield of dihydro-anthracene	
	kg	g	%
Stationary.....	0	6.8	67.3
Moving slowly..	0.15	5.0	49.5
Moving rapidly.	0.5	4.2	11.8
Moving very rapidly.....	1.0	0.0	0.0

3. The Electrolytic Reduction of Sorbic Acid

The catholyte used for electrolysis consisted of a solution of 6 g of sorbic acid in 150 ml of 10% caustic potash. The anolyte was a caustic potash solution of the same concentration. The current density was 26.9 amp per sq. dm; the voltage was 12.5-13 volts; and the temperature was kept at 23-25° by a cooling system. Electrolysis lasted 2 hours. Tests were made of electrolysis with a cathode consisting of stationary mercury and with rapidly renewed mercury in a jet cathode.

The catholyte was treated as follows. The solution was strongly acidified and then extracted three times with 50 ml of ether; the product resulting from desiccation and driving off the ether was distilled in vacuum to recover the mixture of dihydro acids. A fraction with a b.p. of 14° at 23 mm pressure was collected. One part of the resulting product was used to determine the amount of added bromine, the other part being used to determine the amount of added iodine. Starting with the quantities of bromine and iodine absorbed, we determined the amount of caproic acid and $\Delta\alpha$-dihydrosorbic acid and the total $\Delta\beta$- and $\Delta\gamma$-dihydrosorbic acids. The results of these determinations, made as stated above, are given in Table 7.

TABLE 7

Cathode	Resulting products							
	Distillate with b.p. of 140° (23 mm), dihydrosorbic acids, and caproic acid, g	Added bromine, g	Corresponding quantity of dihydro acids, g	Added iodine, g	Corresponding quantity of $\Delta\alpha$-dihydro acids		$\Delta\beta$- and $\Delta\gamma$-dihydro acids	
					g	%	g	%
Stationary mercury								
Test 1.....	3.12	4.418	3.15	6.484	0.24	4.00	2.91	48.5
Test 2.....	3.54	4.904	3.50	7.146	0.30	4.70	3.20	53.3
Renewed mercury (jet cathode)								
Test 1.....	3.60	4.946	3.53	7.023	0.34	5.70	3.19	53.2
Test 2.....	3.20	4.558	3.25	6.417	0.36	6.00	2.89	48.2

4. The Electrolytic Reduction of Benzoic Acid

In an alkaline medium, 2 g of benzoic acid dissolved in 50 ml of 52% caustic potash was subjected to reduction. The anolyte was a 10% solution of the alkali. Electrolysis was effected with a current density of 6.3 amp per sq dm, a voltage of 15 volts, and a temperature of 40°. Electrolysis lasted 1 hour. The catholytes of 3 tests were combined and treated by the Aschan method [7].

In an acid medium, 2 g of benzoic acid dissolved in 27.5 ml of 96% ethyl alcohol was subjected to reduction; 12.5 ml of 30% sulfuric acid and 12.5 ml of water were also added to the solution.

Electrolysis was effected at a current density of 6.3 amp per sq dm, a voltage of 10 volts, and a temperature of 25°. Electrolysis lasted 1 hour. The combined catholytes of three tests were treated together.

The results of these experiments are listed in Table 8.

TABLE 8

Test conditions	Medium							
	Alkaline				Acid			
	Yield				Yield			
	Hydrobenzoic acids		Benzyl alcohol		Hydrobenzoic acids		Benzyl alcohol	
	g	%	g	%	g	%	g	%
Stationary mercury.....	4.5	76.0	0.48	8.0	–	–	1.506	25.1
Rapidly renewed mercury.	–	–	–	–	–	–	1.494	24.9

5. Production of Glyoxylic Acid by Electrolytic Reduction of Oxalic Acid

Experiments were run on the reduction of oxalic acid at temperatures of 10 and 25° with a cathode of stationary mercury and of rapidly renewed mercury. 2.2 g of oxalic acid in 40 ml of 15% sulfuric acid was used in each test. Electrolysis was continued for 30 minutes at a current density of 6 amp per sq dm and a voltage of 5 volts. Three tests were run in each series.

The amount of glyoxylic acid was determined iodometrically. The results obtained in each series of tests are listed in Table 9.

TABLE 9

Test conditions	Temperature 10°			Temperature 25°		
	Yield, g	Average, g	%	Yield, g	Ave. g	%
Stationary mercury..	0.43, 0.44, 0.45	0.44	20	0.60, 0.58, 0.59	0.59	26.9
Rapidly renewed mercury.....	0.65, 0.66, 0.67	0.66	30	0.60, 0.59, 0.61	0.60	27.3

SUMMARY

1. As a cathode material, mercury may exhibit catalytic action in the electrolytic reduction process, though not in every instance.

2. This is related to the differing effect of renewing the cathode mercury upon the process of electrolytic reduction.

Case 1. If the catalytic action of the cathode material is required, in addition to a given value of the cathode potential, for the reduction of the depolarizer (depending upon the nature of the latter) and mercury exhibits this action, the continuous reduction of the cathode mercury promotes the reduction process.

Case 2. If the mercury does not exhibit a catalytic action, the reaction that occurs in an alkaline medium at a mercury cathode that is not renewed (i.e., at an amalgam) ceases when the renewal of the mercury is rapid enough.

Case 3. If, depending upon the nature of the depolarizer, only a given value of the cathode potential is required for reducing it, renewing the cathode mercury has absolutely no effect upon the reduction process.

3. In Case 1 reactions, using a renewed mercury cathode is useful.

4. In Case 2 reactions, using a renewed mercury (jet) cathode in an alkaline medium makes it possible to eliminate the reduction process entirely. In this manner conditions may be set up for having only anodic processes take place without having recourse to the use of a diaphragm.

5. In Case 3 reactions, there is no advantage in using a renewable mercury cathode.

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THE ELECTROLYTIC HYDROGENATION OF ACETALS WITH A TRIPLE BOND

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The electrolytic hydrogenation of acetals having a triple bond is of practical as well as theoretical interest. No research has been done up to the present on the hydrogenation of triple-bond acetals to double bond ones.

There are several references in the literature [1] to research on simple vinyl ethers. These methods of producing simple vinyl ethers are based upon the reaction of halogen derivatives of hydrocarbons with alcoholates or alcohols in organic solvents in the presence of alkalies. But all these methods of producing simple vinyl ethers were not widely employed in the chemical industry.

In 1888, A.E.Favorsky [2], in his research on the isomeric conversions of acetylenic hydrocarbons, found that alcohols condense with acetylenic hydrocarbons in the presence of alkalies. This paper by A.E.Favorsky stimulated numerous researches in this field [3].

A recent and original method for producing simple vinyl ethers is the method worked out by A.E.Favorsky and M.F.Shostakovsky [4]. This method is based on the reaction of acetylene with alcohols in the presence of highly alkaline catalysts. In addition to the vinyl ethers, various vinyl acetals [5] can be synthesized by reacting vinyl ethers or α-chloro ethers with vinyl alcohols.

Several researchers have found [6] that the chlorine in α-chloro ethers, where the halogen is attached to a carbon atom of the alkoxy group, is extremely active. These α-chloro ethers react readily with alcohols, forming acetals, as well as with tertiary amines, forming quaternary ammonium salts, which in turn react even more readily with alcohols, as follows:

1. $CH_3-O-CH_2Cl + ROH \longrightarrow CH_3-O-CH_2-O-R + HCl$
2. $CH_3-O-CH_2Cl + NR_3 \longrightarrow [CH_3-O-CH_2-NR_3]^+ \bar{C}l$
3. $[CH_3-O-CH_2-NR_3]^+ \bar{C}l + ROH \longrightarrow CH_3-O-CH_2O-R + [HNR_3]^+ \bar{C}l$

With the above-mentioned papers as a basis, I set as my objective the synthesizing of acetals with a triple bond for electrolytic hydrogenation, thus dispensing with the synthesis and identification of the quaternary ammonium salts. I began this research as far back as 1946 [7]. Acetals with a triple bond were produced by reacting α-chloro ethers with acetylene alcohols in absolute ether in the presence of dimethylaniline, quinoline, or powdered caustic soda.

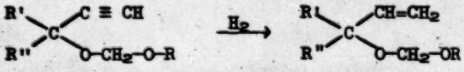
The resulting acetals boil over a wide temperature range. The data in the literature [8] might lead one to assume the disproportionation of the mixed acetal

during the distillation of the resulting products. But when distillation was repeated, we always got a product that boiled within narrow limits and was a chemically homogeneous, individual product according to all indications.

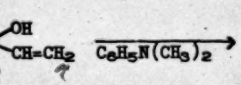
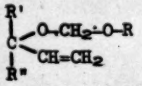
According to the literature [9], acetals decompose into alcohols and ethers upon catalytic hydrogenation. We were interested in learning how triple-bond acetals would behave when they were electrolytically hydrogenated to a double bond.

A.E.Favorsky and his school [10] found that when acetylene alcohols were hydrogenated electrolytically, a molecule of hydrogen is added at the triple bond, resulting as a rule in the formation of vinyl alcohols.

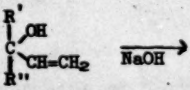
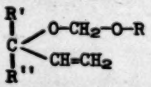
With this as a premise, I began the electrolytic hydrogenation of acetylenic acetals by the method developed by A.E.Favorsky and A.I.Lebedeva [10]. Hydrogenation was effected in accordance with the following equation:



The structure of some of the resulting vinyl acetals was demonstrated by synthesis according to the following reactions:

1. $R\text{-}O\text{-}CH_2Cl$ +  $\xrightarrow{C_6H_5N(CH_3)_2}$ 

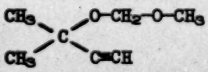
where R, R', R" = CH_3.

2. $R\text{-}O\text{-}CH_2Cl$ +  $\xrightarrow{NaOH}$ 

where R' = CH_3; R, R" = C_2H_5.

EXPERIMENTAL

1) Synthesis of the Methoxy Methyl Ether of Dimethylacetylenylcarbinol:



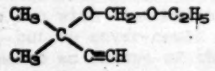
The dimethylacetylenyl carbinol was prepared by the A.E.Favorsky method [11]. 35 g of α-chloro dimethyl ether was added drop by drop in the course of 1.5 hours, with constant stirring and chilling to -10°, to 40 g of dimethylacetylenylcarbinol and 30 g of dimethylaniline, after which stirring was continued for another 3 hours at room temperature. Two layers were formed. The upper layer was separated from the lower one, washed with a weak solution of hydrochloric acid and then with water, and desiccated above Na_2SO_4.

The yield of the methoxy methyl ether of dimethylacetylenylcarbinol was 14 g (i.e., 22.97%, based on the alcohol used). B.p. = 109-112°. The resulting acetylenic acetal turns yellow in storage, has a pleasant odor, and yields a characteristic copious white precipitate with ammoniacal silver nitrate.

d_{28}^{28} 0.8909; n_D^{20} 1.4250; MR_D 36.72.

$C_7H_{12}O_2$F . Computed: MR_D 35.81.
0.2575 g substance: 18.18 g benzene: Δ t 0.57°.
0.2214 g substance: 18.18 g benzene: Δ t 0.47°.
Found: M 127.2, 132.66.
$C_7H_{12}O_2$. Computed: M 128.
0.1076 g substance: 0.2580 g CO_2; 0.0990 g H_2O.
0.2063 g substance: 0.4920 g CO_2; 0.1980 g H_2O.
Found %: C 65.39, 65.00; H 10.22, 10.66.
$C_7H_{12}O_2$. Computed %: C 65.62; H 9.37.

2) Synthesis of the Ethoxy Methyl Ether of Dimethylacetylenylcarbinol:



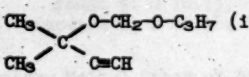
40 g of α-chloro methyl ethyl ether was added in the course of an hour and a half, with constant stirring and chilling to -8°, to 52 g of dimethylacetylenylcarbinol and 26 g of dimethylaniline. The whole was then stirred for another two hours at room temperature. Two layers were formed in the reaction flask. The upper layer was separated from the lower one. The lower layer was extracted with ether. The extract was added to the upper layer, which was washed with a weak solution of hydrochloric acid and three times with water, and then desiccated above Na_2SO_4.

The yield of the ethoxy methyl ether of dimethylacetylenylcarbinol was 24.5 g (or 27.87%, based on the alcohol used). B.p. 120-122°. The resulting acetal turns yellow quickly in storage, has a pleasant odor, and yields a characteristic copious white precipitate with ammoniacal silver nitrate.

d_{20}^{20} 0.8816; n_D^{20} 1.4206; MR_D 40.79.

$C_8H_{14}O_2$F . Computed: MR_D 40.42.
0.2168 g substance: 18.16 g benzene: Δ t 0.46°.
0.1264 g substance: 18.16 g benzene: Δ t 0.24°.
Found: M 132.87, 148.48.
$C_8H_{14}O_2$. Computed: M 142.
0.1106 g substance: 0.2746 g CO_2; 0.1086 g H_2O.
0.1114 g substance: 0.2742 g CO_2; 0.1100 g H_2O.
Found %: C 67.71, 67.12; H 10.91, 10.97.
$C_8H_{14}O_2$. Computed %: C 67.60; H 9.85.

3) Synthesis of the Isopropoxy Methyl Ether of Dimethylacetylenylcarbinol:



35 g of α-chloro methyl isopropyl ether was added, with constant stirring and chilling to -8°, to 40 g of dimethylacetylenylcarbinol and 20 g of dimethylaniline in the course of one hour. Then the reaction mixture was stirred for another 3½ hours at room temperature. 300 ml of water was then added to the contents of the flask. The aqueous solution was extracted with ether and desiccated above Na_2SO_4.

The yield of the isopropoxy methyl ether of dimethylacetylenylcarbinol was 19 g, or 25.57%, based on the alcohol used. B.p. 131-135°. The resulting acetal has a pleasant odor, turns yellow upon storage, and yields a characteristic white

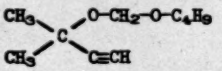
precipitate with ammoniacal silver nitrate.

d_{28}^{28} 0.8682; n_D^{20} 1.4111; MR_D 44.58.
$C_9H_{16}O_2F$. Computed: MR_D 45.04.

0.1465 g substance: 19.23 g benzene: Δt 0.25°.
0.2012 g substance: 19.23 g benzene: Δt 0.35°.
Found: M 156.02, 153.05.
$C_9H_{16}O_2$. Computed: M 156.
0.2101 g substance: 0.5304 g CO_2; 0.2017 g H_2O.
0.1022 g substance: 0.2592 g CO_2; 0.0926 g H_2O.
Found %: C 68.83, 69.17; H 10.66, 10.07.
$C_9H_{16}O_2$. Computed %: C 69.23; H 10.25.

Eight experiments were run with dimethylaniline, with and without solvents and under varying conditions, but we never could get an acetal yield of more than 27.87%. In all these experiments an excess of the α-chloro ether over the quantity computed theoretically was employed.

4) Synthesis of the Butoxy Methyl Ether of Dimethylacetylenylcarbinol



40 g of α-chloro methyl butyl ether was added drop by drop, with constant stirring and chilling to -8°, to a mixture of 200 ml of absolute ether, 18 g of powdered caustic soda, and 40 g of dimethylacetylenylcarbinol in the course of 3 hours. A copious white precipitate (NaCl) was deposited on the walls. The reaction mixture was left to stand overnight, and the next morning the precipitate was filtered out, and the filtrate desiccated over Na_2SO_4. The yield of the butoxy methyl ether of dimethylacetylenylcarbinol was 13 g, or 16.06%, based on the alcohol used; its b.p. was 148-152°.

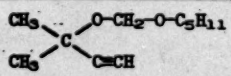
The synthesized acetylenic acetal has a pleasant odor and forms a characteristic copious white precipitate with ammoniacal silver nitrate.

d_{28}^{28} 0.8602; n_D^{20} 1.4150; MR_D 49.48.

$C_{10}H_{18}O_2F$. Computed: MR_D 49.66.

0.1236 g substance: 16.24 g benzene: Δt 0.24°.
0.2320 g substance: 16.24 g benzene: Δt 0.44°.
Found: M 162.36, 166.23.
$C_{10}H_{18}O_2$. Computed: M 170.
0.1112 g substance: 0.2884 g CO_2; 0.1086 g H_2O.
0.1128 g substance: 0.2908 g CO_2; 0.1100 g H_2O.
Found %: C 70.73, 70.30; H 10.85, 10.83.
$C_{10}H_{18}O_2$. Computed %: C 70.58; H 10.58.

5) Synthesis of the Pentoxy Methyl Ether of Dimethylacetylenylcarbinol



22 g of α-chloro methyl isoamyl ether was added, with constant stirring and chilling, to a mixture of 150 ml of absolute ether, 9 g of powdered caustic soda, and 20 g of dimethylacetylenylcarbinol in the course of one hour. A white precipitate was at once thrown down on the walls of the flask. The reaction mixture was then stirred for another four hours at room temperature. Then the contents of the flask were diluted with 200 ml of water, the ether layer was separated

from the aqueous solution, and the latter was extracted with ether. The combined ether extracts were desiccated above calcined Na_2SO_4. The yield was 8.5 g (or 19.4%); b.p. 159-161°.

The synthesized acetal has the odor of ether and forms a copious white precipitate with ammoniacal silver nitrate. It turns yellow rapidly upon storage.

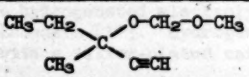
d_{20}^{20} 0.8502; n_D^{20} 1.4109; MR_D 53.72

$C_{11}H_{20}O_2F$. Computed: MR_D 54.28.

0.1488 g substance: 19.72 g benzene: Δt 0.21°.
0.2140 g substance: 18.90 g benzene: Δt 0.32°.
Found: M 184.90, 173.64.
$C_{11}H_{20}O_2$. Computed: M 184.
0.2238 g substance: 0.5872 g CO_2; 0.2282 g H_2O.
0.1952 g substance: 0.5114 g CO_2; 0.1976 g H_2O.
Found %: C 71.55, 71.45; H 11.32, 11.24.
$C_{11}H_{20}O_2$. Computed %: C 71.73; H 10.87.

A total of six experiments was run with powdered caustic soda, using an excess of the α-chloro ether, but we were unable to raise the yield above 19.4%. Apparently, under these conditions the yield drops as the molecular weight of the alpha chloro ethers increases.

6) Synthesis of the Methoxy Methyl Ether of Methylethylacetylenylcarbinol



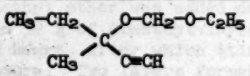
The methylethylacetylenylcarbinol was synthesized by the method originated by Academician A.E.Favorsky [11]. 50 g of α-chlorodimethyl ether was added, at room temperature and with constant stirring, to a mixture of 200 ml of absolute ether, 55 g of methylethylacetylenylcarbinol, and 45 g of quinoline in the course of an hour and a half. A half an hour later yellow crystals, which turned white upon standing, appeared on the walls of the flask. After stirring for four more hours, the reaction mixture was set aside to stand overnight. The next day the contents of the flask were diluted with 300 ml of water, the ether layer was separated, and the aqueous solution was again extracted with ether. The combined extracts were desiccated above Na_2SO_4. The yield of the acetylenic acetal was 27.7 g (or 29.80%). B.p. 132-135°.

The synthesized acetylenic acetal has a pleasant odor, forms a characteristic white precipitate with ammoniacal silver nitrate, and turns yellow upon standing.

d_{20}^{20} 0.8887; n_D^{20} 1.4208; MR_D 40.46;
$C_8H_{14}O_2F$. Computed MR_D 40.42.

0.2334 g substance; 18.42 g benzene: Δt 0.48°.
Found: M 135.15.
$C_8H_{14}O_2$. Computed: M 142.
0.2264 g substance: 0.5582 g CO_2; 0.1986 g H_2O.
Found %: C 67.24; H 9.74.
$C_8H_{14}O_2$. Computed %: C 67.60; H 9.85.

7) Synthesis of the Ethoxy Methyl Ether of Methylethylacetylenylcarbinol



57 g of α-chloro methyl ethyl ether was added, with constant stirring at room temperature, to a mixture of 250 ml of absolute alcohol, 50 g of quinoline, and 64 g of methylethylacetylenylcarbinol in the course of 2 hours. Stirring was stopped after six hours had passed, and the ether solution in the flask was decanted and desiccated above Na_2SO_4.

The yield of the ethoxy methyl ether of methylethylacetylenylcarbinol was 34.8 g (or 29.28%); b.p. 147-150°. The acetal has a pleasant odor, forms a copious white precipitate with ammoniacal silver nitrate, and turns yellow upon standing.

d_{28}^{28} 0.8809; n_D^{20} 1.4266; MR_D 45.43.

$C_9H_{16}O_2$. Computed: MR_D 45.04.

0.2236 g substance: 20.14 g benzene: Δt 0.36°.
Found: M 157.89.
$C_9H_{16}O_2$. Computed: M 156.
0.3106 g substance: 0.7892 g CO_2; 0.3034 g H_2O.
Found %: C 69.28; H 10.85.
$C_9H_{16}O_2$. Computed %: C 69.23; H 10.25.

8) The electrolytic hydrogenation of acetylenic acetals

The initial products, i.e., the acetylenic acetals, were prepared as described above, by reacting α-chloro ethers with acetylenic alcohols.

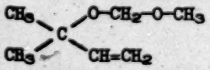
These acetals were hydrogenated electrolytically by the method developed by A.E.Favorsky and A.I.Lebedeva [10]. Hydrogenation was too slow with a copper cathode, but was faster with a silver-plated cathode.

All the synthesized acetylenic acetals were electrolytically hydrogenated with a silverplated copper cathode. Nickel wire was employed as the anode. The anolyte was separated from the catholyte by a porous cylinder. The cathode region was filled with a 1% aqueous-alcoholic solution of caustic soda and the acetylenic acetal. The anode region was filled with a saturated solution of caustic soda.

The hydrogenation process was checked occasionally by taking samples from the electrolyzer and testing for the triple bond. Until hydrogenated, the aqueous-alcoholic solution of the acetal yielded a copious white precipitate with ammoniacal silver nitrate. After the theoretical quantity of hydrogen had been absorbed, the water-alcohol solution of the acetal still caused a white turbidity with ammoniacal silver nitrate, but this turbidity disappeared after hydrogenation. The water-alcohol solution of the acetal, as well as the pure acetal, decolorizes a weak $KMnO_4$ solution and bromine water after hydrogenation. The disappearance of the initial copious white precipitate with ammoniacal silver nitrate and the decolorization of the weak solution of $KMnO_4$ and of the bromine water clearly indicates that the triple bond has been turned into a double bond.

The principal constants of the resulting vinyl acetals are listed in the subjoined table.

9) Synthesis of the Methoxy Methyl Ether of Dimethylvinyl Carbinol



30 g of α-chloro dimethyl ether was added drop by drop, with constant stirring and chilling to -6°, to 32 g of dimethylvinylcarbinol and 24 g of dimethylaniline in the course of 2 hours, after which stirring was continued at room temperature for another 3.5 hours. Two layers formed in the reaction flask after

Serial No.	Formula	B.P.	d_{20}^{20}	n_D^{20}	MR_D		Molecular wt.		Analysis				Acetal yield, %
					Found	Computed	Found	Comp.	Found		Computed		
									C	H	C	H	
1	CH_3, CH_3, C, $O-CH_2-O-CH_3$, $CH=CH_2$	100-104°	0.8626	1.4160	37.81	37.34	133.31	130	64.18	11.27	64.61	10.77	42.19
2	CH_3, CH_3, C, $O-CH_2-O-C_2H_5$, $CH=CH_2$	105-108	0.8525	1.4125	42.07	41.96	135.13	144	66.37	11.20	66.66	11.11	52.18
3	CH_3, CH_3, C, $O-CH_2-O-C_3H_7$ (iso), $CH=CH_2$	119-123	0.8381	1.4114	46.84	46.58	153.62	158	70.33	11.18	68.35	11.39	46.48
4	CH_3, CH_3, C, $O-CH_2-O-C_4H_9$, $CH=CH_2$	132-135	0.8312	1.4090	51.15	51.19	162.09	172	69.87	10.98	69.76	11.62	54.37
5	CH_3, CH_3, C, $O-CH_2-O-C_5H_{11}$ (iso), $CH=CH_2$	148-151	0.8218	1.4095	56.00	55.81	187.48	186	70.50	11.21	70.96	11.82	48.35
6	CH_3, C_2H_5, C, $O-CH_2-O-CH_3$, $CH=CH_2$	121-124	0.8612	1.4120	41.59	41.96	141.02	144	66.44	11.23	66.66	11.11	32.88
7	CH_3, C_2H_5, C, $O-CH_2-O-C_2H_5$, $CH=CH_2$	136-140	0.8516	1.4190	46.84	46.58	159.94	158	68.75	11.55	68.35	11.39	55.01

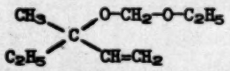
this time had elapsed. The upper layer was separated from the lower one, washed with highly diluted hydrochloric acid and then washed twice with water, and desiccated above Na_2SO_4.

Most of the synthesized vinyl acetal boiled at 108-111° after double distillation. It is a transparent liquid with a pleasant odor, which does not change upon standing.

d_{20}^{20} 0.8612; n_D^{20} 1.4158; MR_D 37.87.

$C_7H_{14}O_2$. Computed: MR_D 37.34.

10) Synthesis of the Ethoxy Methyl Ether of Methylethylvinylcarbinol



46 g of α-chloro methyl ethyl ether was added drop by drop during 2.5 hours with constant stirring and chilling to -8°, to a mixture of 250 ml of absolute ether, 21 g of powdered caustic soda, and 42 g of methylethylvinylcarbinol in a round-bottomed flask fitted with a reflux condenser and a dropping funnel. This causes a copious white precipitate (NaCl) to form in the reaction flask. Four hours later, the precipitate was filtered out of the flask contents, and the filtrate was desiccated above Na_2SO_4.

Most of the synthesized vinyl acetal boiled at 137-140°.

d_{20}^{20} 0.8496; n_D^{20} 1.4184; MR_D 47.00.

$C_9H_{18}O_2$. Computed: MR_D 46.58.

Thus it was found that the electrolytic hydrogenation of acetylenic acetals yields stable vinyl acetals, which have a pleasant odor and have physical and chemical properties that differ sharply from those of acetylenic acetals.

When we compare our data on the electrolytic hydrogenation of the vinyl acetals and of the vinyl alcohols, there doubtless is some common pattern existing between them, but discrepancies are also present. This will be dealt with in my following paper.

SUMMARY

1. A method has been developed for synthesizing acetylenic acetals, and seven new compounds, not described in the literature, have been synthesized.

2. In synthesizing the acetylenic acetals, it has been found that under the given conditions the acetal yield decreases as the molecular weight of the α-chloro ethers used rises.

3. The method developed by A.E.Favorsky and A.I.Lebedeva proved to be fully satisfactory for the electrolytic hydrogenation of acetylenic acetals.

Seven vinyl acetals, not described in the literature, have been synthesized in this manner.

4. It has been found that the less stable acetylenic acetals become more stable when electrolytically hydrogenated to ethylenic acetals.

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ALLYL REARRANGEMENTS

XIII. SYNTHESIS OF MERCAPTANS OF THE ALLYL TYPE AND THEIR TRANSFORMATION INTO THIO ETHERS

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There are few references in the literature to the synthesis of allyl mercaptans. Allyl mercaptan, first synthesized by Hofmann [1] and then by Braun [2] has been described as has been methallyl mercaptan by Tamele, Ott, Mulple, and Hearne [3].

In one of our preceding papers [4] we made a study of the action of sodium hydrosulfide upon isomeric methoxychloropentenes, a dimethoxy pentenyl thio ether being secured, in the main, in both cases instead of the expected mercaptans. It was supposed that the thio ethers are formed by the reaction of a mercaptan with a chloride; a primary chloride reacts normally, while a secondary chloride causes a complete allyl rearrangement.

The objective of the present paper is a further study of the reactions between isomeric alkoxychloropentenes and hydrosulfides of the metals, with special attention to an effort to explain the possibility of synthesizing mercaptans from them and to a study of the mechanism by which the thio ethers are formed. This research was done with the isomeric methoxy-, ethoxy-, and butoxychloropentenes and the 1,2- and 1,4-dichlorobutenes. A study of the effect of the reaction conditions upon the formation of a mercaptan and of thio ethers was made with primary ethoxychloropentene as an example.

When this primary ethoxychloropentene was reacted with sodium hydroxysulfide prepared by the Tiede and Rânicke method – heating in absolute alcohol, we got two fractions, corresponding to ethoxypentenylthiol and diethoxypentenylthio ether, with total yields of 32% and 20% respectively. Redistillation of these fractions yielded primary ethoxypentenylthiol, with a b.p. of 70-71° (6 mm); n_D^{20} 1.4725; d_4^{20} 0.9530; and diethoxypentenylthiol ether, with a b.p. of 172-175°. (12 mm); n_D^{20} 1.4830; d_4^{20} 0.9464. The structure of the ethoxypentenylthiol was borne out by oxidizing it with potassium permanganate; a yield of 17.5% of β-ethoxypropionic acid was obtained.

Hence, the formation of ethoxypentenylthiol proceeds in accordance with the normal equation:

$$C_2H_5OCH_2CH_2CH{=}CHCH_2Cl + {}^{-}SH \longrightarrow C_2H_5OCH_2CH_2CH{=}CHCH_2SH + Cl^{-}.$$

In fractionating the mercaptan fraction, we noticed that part of the mercaptan was converted into a thio ether. That is why subsequent experiments on the synthesis of the mercaptans were made in the cold, with the alcohol being driven off from the reaction mixture and the subsequent fractionation of the reaction products

being effected in vacuum at as low a temperature as possible. Under these conditions the yield of ethoxypentenylthiol rose to 40%, and that of the thio ether to 13%.

It was later found that 80-90% alcohol and caustic potash could be successfully employed to prepare the hydrosulfide instead of sodium alcoholate in absolute alcohol. When the reaction conditions specified above are observed, the mercaptan yield was raised to 52%; the thio ether yield was 15%. We were unable to recover noticeable quantities of the mercaptan and the thio ether when the reaction was effected with aqueous solutions of sodium and potassium hydrosulfide with vigorous stirring of the reaction mixture, whether in the cold or when heated. Most of the chloride was recovered from the reaction unchanged. The reaction of the secondary ethoxychloropentene with sodium hydrosulfide in alcohol does not take place without the application of heat, owing to its low reactivity. When heat is applied, it is chiefly the thio ether that is formed, plus an extremely minute quantity of a mercaptan whose constants indicate that it is identical with that secured from the primary ethoxychloropentene. This indicates that in this latter case the reaction entails a complete allyl rearrangement as follows:

$$C_2H_5OCH_2CH_2\underset{Cl}{C}H-CH=CH_2 \longrightarrow \left[\begin{array}{l} C_2H_5OCH_2CH_2CH=CH-\overset{+}{C}H_2 \\ \downarrow \quad\quad\quad \uparrow \\ C_2H_5OCH_2CH_2\overset{+}{C}H-CH=CH_2 \end{array}\right] + \bar{S}H \longrightarrow C_2H_5OCH_2CH_2CH=CH-CH_2SH + \bar{C}l$$

As has already been set forth above, part of the ethoxypentenylthiol is converted into diethoxypentenylthio ether when it is distilled in vacuum. In order to investigate this interesting and hitherto unknown reaction, we heated the mercaptan for many hours at 100° and 130°. The refractive index of the reaction mixture was measured at definite intervals of time. It was found that the refractive index increased sharply during the first few hours, the rise gradually slowing down during further heating. Fractionation of the mixture after heating indicated that the ratio of the mercaptan to the thio ether, computed from the fractionation data, was higher than the ratio computed from the refractive indexes. This is due to the fact that when the mercaptan is heated, other reactions involving the oxidation and the polymerization of the mercaptan [2] take place in addition to its conversion into the thio ether. The fractionation residue has a much higher refractive index than the thio ether, while its sulfur percentage is somewhat higher than the computed value for di-(ethoxypentenyl)-disulfide. Eight hours of heating the ethoxypentenylthiol to 130° yielded a mixture of products, which fractionation indicated contained 49% of the mercaptan, 35% of the thio ether, and 16% of the residue.

The principal reaction occurring when ethoxypentenylthiol is heated is, therefore, its conversion into a thio ether.

$$2C_2H_5OCH_2CH_2CH=CHCH_2SH \longrightarrow C_2H_5OCH_2CH_2CH=CHCH_2-S-CH_2CH=CHCH_2CH_2OC_2H_5 + H_2S.$$

The hydrogen sulfide evolved when the mercaptan is heated was detected by the characteristic precipitate of lead sulfide.

It is noteworthy that octylthiol remained unchanged when it was heated under the same conditions, as was demonstrated by measuring the refractive index and by its fractionation after heating was completed.

Our results enable us to conclude that the presence of a double bond at the β,γ-position with respect to the carbon atom attached to the SH group greatly increases the latter's reactivity.

The reaction of primary butoxychloropentene with sodium hydrosulfide in the cold in 90% alcohol resulted in the recovery of 42.5% of primary butoxypentenylthiol, with a b.p. of 107-110° (11 mm); n_D^{20} 1.4675; d_4^{20} 0.9230; and 22.5% of

dibutoxypentenylthio ether, with a b.p. of 185-187° (5 mm); n_D^{20} 1.4785; d_4^{20} 0.9204.

When butoxypentenylthiol was refractionated in vacuum, it, too, was partially converted into dibutoxypentenylthio ether, which was isolated and identified by its constants. Secondary butoxychloropentene reacts with sodium hydrosulfide only when heated, yielding chiefly the thio ether and a small quantity of a mercaptan, the constants of which indicate that it is identical with that secured from the primary chloride. In the case of the butoxychloropentenes, therefore, the reactions are likewise normal for the primary chloride and wholly abnormal for the secondary chloride.

The picture was similar for the isomeric methoxychloropentenes. In the case of the primary methoxychloropentene, we got practically nothing but the primary methoxypentenylthiol, with a b.p. of 63-67° (7 mm); n_D^{20} 1.4775; d_4^{20} 0.9783 (yield of 55%), with merely a minute quantity of a higher fraction whose boiling point was much below that of the thio ether. When the methoxypentenylthiol is heated, it, too, is partially converted into a thio ether. In the case of the secondary methoxychloropentene, the reaction was carried out with heating; this yielded a small quantity of the primary ethoxypentenylthiol and a much larger quantity of the thio ether.

To determine the general nature of the transformation of allyl mercaptans into the corresponding thio ethers at higher temperatures, we synthesized and heated allylthiol; we also found that part of it was converted into a thio ether.

The reactions of isomeric dichlorobutenes with potassium hydrosulfide are complicated, yielding a mixture of products that boils throughout a wide temperature range; we were unable to recover any substances with fixed boiling points from this mixture.

EXPERIMENTAL

Action of sodium and potassium hydrosulfide on 1-ethoxy-5-chloropentene-3. 5 g of sodium was dissolved in 100 ml of absolute ethyl alcohol. The solution was saturated with anhydrous hydrogen sulfide for 5 hours. Then 25 g of 1-ethoxy-5-chloropentene-3 was added, and the reaction mixture was heated over a water bath for 3 hours. The precipitate that settled was filtered out, the alcohol was driven off, and the residue was diluted with water and extracted with ether. The ether extract was desiccated above calcium chloride, the ether was driven off, and the residue was fractionated in vacuum. Fractionation yielded 8 g of a fraction with a boiling point of 82-87° (14 mm) and 4.8 g of a fraction with a boiling point of 170-185° (14 mm). Refractionation of these fractions yielded: 1-ethoxypentene-3-thiol-5, with a b.p. of 70-71° (6 mm); n_D^{20} 1.4725; d_4^{20} 0.9530:

0.1172 g substance: 0.1833 g $BaSO_4$ (Carius).
Found %: S 21.60.
$C_7H_{14}OS$. Computed %: S 21.92.

and diethoxypentenylthio ether, with a b.p. of 172-175° (12 mm); n_D^{20} 1.4830; d_4^{20} 0.9460.

0.1376 g substance: 0.1284 g $BaSO_4$ (Carius).
Found %: S 12.78.
$C_{14}H_{28}O_2S$. Computed %: S 12.43.

During fractionation of the mercaptan fraction it was noticed that part of the mercaptan changes into a thio ether, which distils at 173-176° (12 mm).

Fractionation of the residue yielded 1.2 g of a fraction that boiled with

The yields of the mercaptan and the thio ether given in the theoretical section of this paper were computed from the results of the initial fractionation in this and other experiments.

decomposition within the 190-207° range (6 mm).

0.1202 g substance: 0.1996 g $BaSO_4$ (Carius)
Found %: S 22.70.
$C_{14}H_{28}O_2S_2$. Computed %: S 22.07.

In another experiment using the same quantities of reagents, the reaction mixture was allowed to stand without heating for twenty-four hours, after which the alcohol was driven off in vacuum at 30°. Fractionation of the residue yielded 10.1 g of the mercaptan and 3.9 g of the thio ether.

When the reaction was performed analogously with potassium hydrosulfide, prepared by passing hydrogen sulfide through a water-alcohol solution of caustic potash (9.8 g of KOH, 100 ml of 80% alcohol, and 20 g of the chloride), it yielded 10.2 g of the mercaptan and 3 g of diethoxypentenylthio ether.

Action of sodium hydrosulfide upon 1-ethoxy-3-chloropentene-4. 5 g of sodium was dissolved in 100 ml of absolute alcohol, and the resulting alcoholate solution was saturated for 5 hours with hydrogen sulfide. Then 25 g of 1-ethoxy-3-chloropentene-4 was added, and the mixture was set aside to stand overnight at room temperature. No precipitate was thrown down. The reaction mixture was heated for 3 hours over a water bath. A copious precipitate of sodium chloride settled out. The alcohol was driven off, and the residue was treated with water and extracted with ether. After the ether had been driven off, the residue was fractionated in vacuum. This yielded 3.2 g of 1-ethoxypentene-3-thiol-5, with a b.p. of 70-71° (6 mm); n_D^{20}1.4730; and 7.6 g of diethoxypentenylthio ether with a b.p. of 176° (12 mm); n_D^{20}1.4825. No noticeable quantity of lower-boiling fractions was recovered. Refractionation of the mercaptan yielded a small quantity of a thio ether with a b.p. of 174-177° (12 mm).

Experiments on heating 1-ethoxypentene-3-thiol-5. 10 g of 1-ethoxypentene-3-thiol-5 was heated to 85° in a small flask over a water bath. The refractive index of the reaction mixture was measured at regular intervals of time. The refractive index changed from 1.4718 to 1.4792 as the result of 13 hours of heating.

Fractionation of the reaction mixture yielded 4.75 g of the original mercaptan and 1.85 g of diethoxypentenylthio ether, with a b.p. of 160-165° (7 mm); n_D^{20} 1.4810. The residue was approximately 1 g; n_D^{20} 1.5050. In a second experiment, 10 g of 1-ethoxypentene-3-thiol-5 was heated for 8 hours to 130° over an oil bath. After heating was complete, fractionation of the reaction mixture yielded 4.7 g of the original mercaptan and 3.3 g of diethoxypentenylthio ether, with a b.p. of 170-174° (8 mm); n_D^{20}1.4815. The fractionation residue amounted to approximately 1.5 g; n_D^{20} 1.5055; sulfur content 26.8%.

To absorb the hydrogen sulfide evolved in the reaction, a small outlet tube leading from the reaction flask in which the mercaptan was heated was immersed in a solution of lead acetate. A black precipitate of lead sulfide, insoluble in cold dilute nitric acid but soluble in the hot acid, was observed to form.

Oxidation of 1-ethoxypentene-3-thiol-5 by potassium permanganate. 60.6 g of pulverized potassium permanganate was gradually added, with constant stirring, to a mixture of 10 g of the mercaptan in 1000 g of water. The reaction mixture was cooled by circulating water while the permanganate was added. After standing for a day, the solution was decolorized above manganese dioxide. The manganese dioxide was filtered out and washed repeatedly with hot water. The filtrate was concentrated and treated with hydrochloric acid. The resulting solution, with the layer of oil floating on its surface, was extracted repeatedly with ether, the ether extract was desiccated above calcium chloride, the ether was driven off, and the residue was fractionated in vacuum. This yielded 1.4 g of β-ethoxypropionic acid, with a b.p. of 109° (13 mm) and n_D^{20}1.4215.

Oxidation of diethoxypentenylthio ether by potassium permanganate. Oxidation of 10 g of the thio ether required 39.2 g of potassium permanganate. The oxidation process and the treatment of the reaction mixture were similar to those in the preceding experiment.

Fractionation of the oxidation products yielded 2.6 g of ethoxypropionic acid, with a b.p. of 110° (13 mm); n_D^{20} 1.4205; d_4^{20} 1.0430. Found: MR_D 28.60. $C_5H_{10}O_3$. Computed: MR_D 28.47. The constants given in the literature for ethoxypropionic acid are: b.p. 108° (10 mm); d_4^{20} 1.0461.

Heating octylthiol. The octylthiol was synthesized from octyl chloride by reacting it with potassium hydrosulfide in a heated alcohol solution. No dioctyl thio ether was noticed; 8.7 g of the octylthiol was heated for 8 hours to 130° over an oil bath. No change in its refractive index occurred during that time. Fractionation of the mixture after it had been heated yielded some 8 g of the original mercaptan.

Action of potassium hydrosulfide on 1-butoxy-5-chloropentene-3. A solution of 9.5 g of caustic potash in 100 ml of 84% alcohol was saturated with hydrogen sulfide for 4 hours. Then 25 g of 1-butoxy-5-chloropentene-3 was added to the solution from a dropping funnel, after which the reaction mixture was set aside to stand for a day. The treatment of the reaction mixture resembled that in the preceding experiments. Fractionation of the reaction products yielded 12 g of a fraction that boiled at 86-100° (4 mm) and 5 g of a fraction that boiled at 160-180° (4 mm). Refractionation of the first fraction yielded: 1-butoxypentene-3-thiol-5 as a colorless liquid with an unpleasant garlic odor and a b.p. of 107-110° (11 mm); n_D^{20} 1.4675; d_4^{20} 0.9232.

0.1818 g substance: 0.2500 g $BaSO_4$ (Carius).
Found %: S 18.89.
$C_9H_{18}OS$. Computed %: S 18.39.

We also secured a minute quantity of a liquid that boiled at a lower temperature (approximately 0.5 g) and some 3 g of a fraction with a b.p. of 180-185° (6 mm).

Refractinnation of the second fraction yielded dibutoxypentenylthio ether as a light-brown liquid with an unpleasant odor and a b.p. of 185-187° (6 mm); n_D^{20} 1.4770; d_4^{20} 0.9204.

0.2170 g substance: 0.1186 g $BaSO_4$ (Carius).
Found %: S 9.79.
$C_{18}H_{34}O_2S$. Computed %: S 10.19.

Action of potassium hydrosulfide upon 1-butoxy-3-chloropentene-4. 19 g of caustic potash was dissolved in 200 ml of 84% ethyl alcohol, and hydrogen sulfide was then passed through the solution for 4 hours. Then 50 g of 1-butoxy-3-chloropentene-4 was added to the reaction mixture, which was set aside to stand for a day at room temperature. No precipitate of potassium chloride settled out. The reaction mixture was heated for 3 hours over a water bath. A copious precipitate settled out; the alcohol was driven off in vacuum, and the residue was treated with water and extracted with ether. After the ether had been driven off (at a slight vacuum), the residue was fractionated in vacuum. This yielded 3.1 g of 1-butoxy-pentenyl-3-thiol-5, with a b.p. of 92-94° (4 mm); n_D^{20} 1.4620, and 17.2 g of dibutoxypentenylthio ether, with a b.p. of 178-182° at 4 mm; n_D^{20} 1.4750.

Action of potassium hydrosulfide upon 1-methoxy-5-chloropentene-3. This experiment was carried out with 25 g of 1-methoxy-5-chloropentene-3 by the procedure described for 1-butoxy-5-chloropentene-3. Treatment and fractionation of the reaction products yielded: 13.4 g of 1-methoxypentene-3-thiol-5, with a b.p. of 63-66° (7 mm); n_D^{20} 1.4775; d_4^{20} 0.9783:

0.1352 g substance: 0.2362 g $BaSO_4$ (Carius)
Found %: S 24.0.
$C_6H_{12}OS$. Computed %: S 24.3.

and 1.1 g of a fraction that boiled at 68-72° (7 mm); n_D^{20} 1.4830.

Action of potassium hydrosulfide upon 1-methoxy-3-chloropentene-4. This experiment was carried out with 20 g of 1-methoxy-3-chloropentene-4 by the procedure described for 1-butoxy-3-chloropentene-4. Fractionation of the reaction products yielded 2 g of a fraction with a b.p. of 69-73° (12 mm); n_D^{20} 1.4782; and 3.4 g of dimethoxypentenylthio ether, with a b.p. of 161° (10 mm); n_D^{20} 1.4940.

Action of potassium hydrosulfide upon allyl bromide. The reaction was carried out with 25 g of allyl bromide by the procedure described for 1-butoxy-3-chloropentene-3. Fractionation of the reaction mixture yielded 9.3 g of a fraction that boiled at 68-85°, and 3.2 g of a fraction that boiled in the 132-145° range.

Refractionation of the first fraction yielded allylthiol, with a b.p. of 63-68°; n_D^{20} 1.4680; d_4^{20} 0.9304 and a small quantity of the thio ether.

Fractionation of the second fraction yielded the pure thio ether, with a b.p. of 138-140°; n_D^{20} 1.4895, which agrees with the constants given for this compound in the literature.

Allylthiol oxidizes and polymerizes very rapidly upon standing. The refractive index of the mercaptan changed from 1.4680 to 1.4900 after standing for 2 days; heavy drops of a polymer, which were insoluble in the allylthiol, were seen to form.

SUMMARY

1. A procedure has been developed for the synthesis of mercaptans or thio ethers by reacting allyl halides with metal hydrosulfides in alcoholic or water-alcohol solutions.

2. It has been proved that allyl mercaptans are transformed by heat into the corresponding thio ethers, according to the equation:

$$2R\text{-}CH{=}CH\text{-}CH_2SH \longrightarrow R\text{-}CH{=}CH\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH{=}CH\text{-}R + H_2S.$$

Alkyl mercaptans are not changed under similar conditions (heating to 100-130°).

3. Primary methoxy-, ethoxy-, and butoxychloropentenes react normally with hydrosulfides of the alkali metals, without rearrangement, but secondary methoxy-, ethoxy-, and butoxychloropentenes react with a complete allyl rearrangement.

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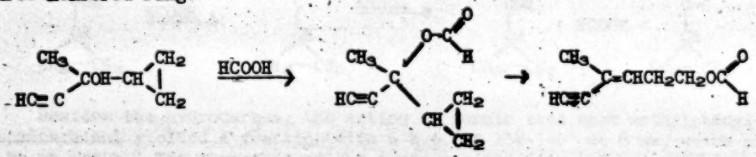
THE TRANSFORMATION OF DERIVATIVES OF ETHYLENIC HYDROCARBONS INTO DERIVATIVES OF THE SIMPLEST POLYMETHYLENIC CYCLES

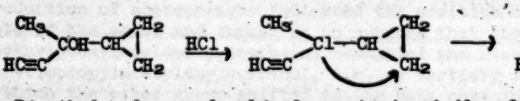
IV. THE REACTION OF METHYLPHENYLALLYLCARBINOL AND METHYLPHENYL- AND METHYLETHYLCYCLOPROPYLCARBINOLS WITH FORMIC ACID

T. A. Favorskaya and the students N. V. Shcherbinskaya and S. E. Chernobelskaya

It has been shown by one of the present authors [1] that the reaction of formic acid with methylcyclopropylacetylenylcarbinol results in the formation of an ester, with an ether group shifting to the β-position and the rupture of the three-membered ring:

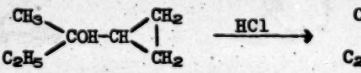


Thus this ester is a primary alkenyne alcohol. The mechanism of its formation is entirely analogous to the mechanism of formation of the primary chlorohydrin, which is produced by reacting methylcyclopropylacetylenylcarbinol with hydrochloric acid:



Dimethylcyclopropylcarbinol reacts in similar fashion with hydrochloric acid [2].

When hydrochloric acid is reacted with methylethylcyclopropylcarbinol, a tertiary chloride results – the chlorohydrin of methylethylallylcarbinol [3]:

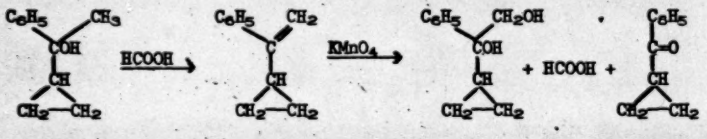


Both of these chlorides – the primary as well as the tertiary – yield the original cyclic alcohols when acted upon by an aqueous solution of potash. The nature of the halogen in the halohydrin has no effect upon the ability of the halide to cyclize when heated with an aqueous potash solution; we have shown [4] that the iodohydrin of methylethylallylcarbinol likewise yields methylethylcyclopropylcarbinol when heated with a 20% potash solution.

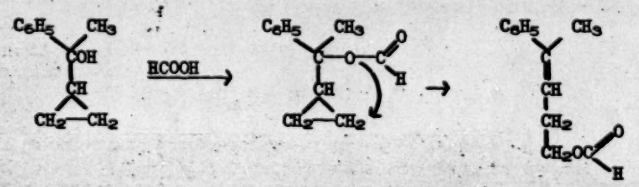
We were interested in making a study of the behavior of the esters of organic

acids of corresponding structure, to learn whether they would also be cyclized when heated with an aqueous potash solution, like the foregoing halides. For this purpose we took the isomeric alcohols methylphenylcyclopropylcarbinol and methylphenylallylcarbinol and investigated their behavior with formic acid. We used methylethylcyclopropylcarbinol as the cyclic alcohol with nothing but aliphatic radicals for the reaction with formic acid.

We found that the reaction of formic acid with methylphenylcyclopropylcarbinol proceeds along two lines: on the one hand, the alcohol is dehydrated, forming the cyclic hydrocarbon α-phenyl-α-cyclopropylethylene, which was first synthesized by N.M.Kizhner [5]; on the other hand, the ester is formed. The constants of the hydrocarbon we had synthesized resembled those given by Kizhner for the hydrocarbon he had synthesized from methylphenylcyclopropylcarbinol by reacting it with acetic anhydride. The structure of the hydrocarbon was proved by oxidizing it with potassium permanganate, benzoyltrimethylene being secured as the neutral product, which was identified as its semicarbazone. Formic acid was found in the volatile acid products; the solution remaining after the formic acid was driven off, yielded a crystalline substance with a m.p. of 53°, which was found to be an intermediate oxidation product – α-phenyl-α-cyclopropylethylene glycol, whose structure was proved by oxidizing it with lead tetraacetate. The resulting benzoyltrimethylene was converted into its semicarbazone.

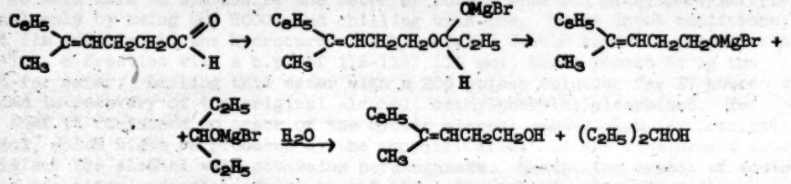


Besides the hydrocarbon, the action of formic acid upon methylphenylcyclopropylcarbinol yielded a fraction with a b.p. of 138-140° at 8 mm, which proved to be an ester. The structure of the ester was demonstrated by oxidizing it with potassium permanganate and then ozonizing it. Acetophenone, identified as its semicarbazone, was secured in both cases. The acid produced was formic acid; no acrylic acid could be found, though it should have been present upon oxidation, inasmuch as its determination was hampered by the presence of formic acid. The production of acetophenone indicated the position of the double bond in the molecule of the ester and forced us to suppose that the reaction of formic acid with methylphenylcyclopropylcarbinol resembled the reaction of formic acid with methylcyclopropylacetylenylcarbinol, i.e., a tertiary ester was formed at first, after which the ether group shifted to the beta position and the ring was ruptured.



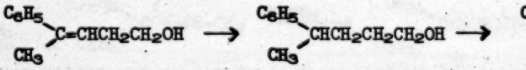
But though the primary chloride thus formed from hydrochloride acid and dimethylcyclopropylcarbinol was readily saponified by a 10% potash solution, yielding a cyclic alcohol:

the ester synthesized by us was not saponified by the action of a 20% potash solution for 20 hours nor by the action of a 20% KOH solution for 64 hours. Hydrolyzing the ester by the Auwers method [6], by reacting it with a water-alcohol solution of NaOH likewise yielded a negative result. In view of this, we resolved to decompose the ester we had synthesized by reacting it with ethylmagnesium bromide, as follows:



This reaction yielded two alcohols. The diethylcarbinol was identified as phenylurethane, while the 2-phenylpenten-2-ol-5 was analyzed and its physical constants were determined. In view of the fact that we failed to recover acrylic acid when we oxidized the ester and thus failed to prove its structure beyond doubt, we decided to hydrogenate the resulting unsaturated alcohol.

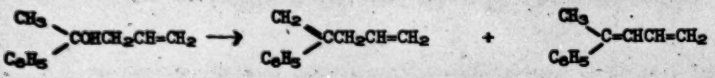
Hydrogenation yielded γ-phenyl amyl alcohol, which was then oxidized to γ-phenylvaleric acid. The synthesis of γ-phenylvaleric acid, which is known in the literature [7], proved beyond doubt that the unsaturated alcohol contained a primary alcohol group and indicated the position of the ether group in the ester produced by the action of formic acid upon methylphenylcyclopropylcarbinol.



Thus, our experiments enable us to assert that the action of formic acid upon methylphenylcyclopropylcarbinol results in formation of an ester of an unsaturated primary alcohol, which cannot be reconverted into the original cyclic alcohol by the action of alkaline agents.

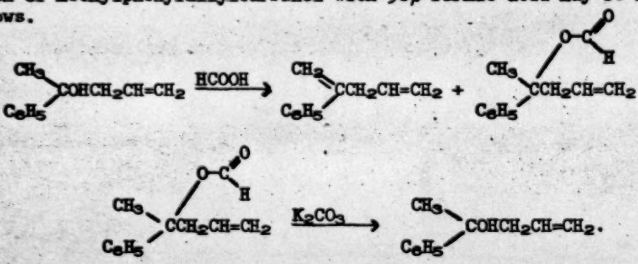
We might have thought that the action of formic acid upon methylphenylallylcarbinol would result in recovery of an ester of this tertiary alcohol. But under the conditions in which the formic acid was reacted with methylphenylcyclopropylcarbinol and methylcyclopropylacetylenylcarbinol we were unable to secure an ester of methylphenylallylcarbinol. The action of 48% HCOOH and heating resulted in the production of a hydrocarbon with an isolated system of double bonds and a small quantity of a polymer, proving that dehydration partly took place at the allyl radical as well, giving rise to a hydrocarbon with conjugated double bonds. This polymer was the sole reaction product when methylphenylallylcarbinol was boiled with 80% formic acid. The polymer was analyzed, but not investigated any further. The hydrocarbon was oxidized by potassium permanganate, the principal reaction products proving to be benzoic and oxalic acids, indicating the presence of isolated double bonds in the hydrocarbon. The negligible quantity of acetophenone found upon oxidation indicates that part of the hydrocarbon with conjugated double bonds was present as the monomer, as an impurity in the hydrocarbon with isolated double bonds.

Thus, the reaction of methylphenylallylcarbinol with formic acid under the foregoing conditions may be represented as follows:



2-phenylpentadiene-1,4 4-phenylpentadiene-1,3

We were able to synthesize the ester of formic acid and methylphenylallylcarbinol only by using 98% HCOOH and chilling with ice. Under these conditions, we got (in addition to the hydrocarbon with isolated double bonds) 2-phenylpentadiene-1,4, a fraction with a b.p. of 112-114° (10 mm), which proved to be the sought-for ester. Boiling this ester with a 20% potash solution for 27 hours resulted in recovery of the original alcohol, methylphenylallylcarbinol. To prove that it contained no trace of the cyclic alcohol, methylphenylcyclopropylcarbinol, which might be produced by the saponification of the unsaturated ester, we oxidized the alcohol with potassium permanganate. Except for traces of acetophenone, no other neutral products were found. Here, again, therefore, we were unable to effect a conversion of the allyl alcohol into a cyclic one. The reaction of methylphenylallylcarbinol with 98% formic acid may be represented as follows.



Methylethylcyclopropylcarbinol was taken as a tertiary alcohol with a cyclopropyl and two aliphatic radicals in the molecule. When this alcohol was reacted with 80% formic acid and heated, we secured a product that had a boiling point 20° below that of the original alcohol, slowly decolorized a solution of $KMnO_4$, had a molecular weight equaling that of methylethylcyclopropylcarbinol, exhibited no reaction for a carbonyl group, and gave a negative result in a Chugaev-Tserevitinov determination of the hydroxyl groups.

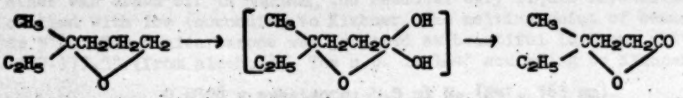
N.D.Zelinsky [8] made a study of the action of oxalic acid upon dimethylcyclopropylcarbinol; he called the resulting product hexylene oxide without giving any proof of this compound's structure. The author attributes the conversion of dimethylcyclopropylcarbinol into a gamma oxide to the successive hydration and dehydration of the alcohol by the oxalic acid.

The properties of the product we had synthesized made us give it the formula of a gamma oxide; it seemed to us to be more likely that the isomerization of methylethylcyclopropylcarbinol into an oxide under the action of formic acid is an intramolecular transformation:

The acid first transforms the cyclopropyl radical into an allyl, after which it shifts the hydrogen of the hydroxyl group to the beta position and closes the oxygen bridge, constituting the oxide.

We had observed the transformation of a cyclopropyl radical into an allyl

earlier [9]. To prove the structure of the synthesized oxide, it was oxidized with potassium permanganate, yielding a lactone of γ-methyl-γ-hydroxycaproic acid:



We titrated the lactone, securing silver γ-methyl-γ-hydroxycaproate; concentrated ammonia in the cold converted the lactone into γ-methyl-γ-hydroxycaproamide. We thus see that the reaction of formic acid with methylethylcyclopropylcarbinol is quite different from its reaction with the alcohols described above, neither a hydrocarbon nor an ester being produced.

EXPERIMENTAL

(By the student N. V. Shcherbinskaya)

I. The Reaction of Methylphenylcyclopropylcarbinol with Formic Acid

Synthesis of methylphenylcyclopropylcarbinol. Methylphenylcyclopropylcarbinol was synthesized by the method developed by Sh. A. Fridman [10]: a mixture of 78.5 g of bromobenzene and 42 g of acetyltrimethylene, dissolved in 250 ml of ether, was added during the course of 4 hours to 12 g of magnesium covered with absolute ether. After decomposition with ice water and dilute sulfuric acid, the reaction products were extracted with ether and desiccated with potash. The residue was distilled in vacuum after the ether had been driven off. Several runs of this reaction yielded 50-55 g of alcohol, with a b.p. of 119-121° at 15 mm. The yield was 53-57%.

The action of 48% and 45% formic acid upon methylphenylcyclopropylcarbinol. 88 g of 48% formic acid was added to 30 g of the alcohol. The reaction mixture was boiled for an hour and a half with a reflux condenser, after which the top layer was separated and then washed with a soda solution and with water. The lower layer was neutralized with soda, after which it was extracted with ether. The residue was desiccated with potash and the solvent was driven off, after which the residue was distilled in vacuum. Two fractions were collected: 1) 88-90° at 8 mm - 12 g (40%); 2) 138-140° at 8 mm: 12.5 g (41%).

The first fraction represented the hydrocarbon phenylcyclopropylethylene, the second being an ester.

In the second experiment, we used a somewhat more dilute acid, containing 45% HCOOH, which raised the output of the ester to 53%, the hydrocarbon yield dropping accordingly.

Analysis of the hydrocarbon with a b.p. of 88-90° at 8 mm:

d_4^{21} 0.9618; n_α^{21} 1.5421; MR_α 47.13.

$C_{11}H_{12}$. Computed: MR_α 47.06.
0.1079 g substance: 0.3616 g CO_2; 0.0790 g H_2O.
0.0914 g substance: 0.3064 g CO_2; 0.0674 g H_2O.
Found %: C 91.39, 91.42; H 8.19, 8.25.
$C_{11}H_{12}$. Computed %: C 91.67; H 8.33.
0.0945 g substance: 14.32 g benzene: Δt 0.23°.
Found: M 146.9.
$C_{11}H_{12}$. Computed: M 144.0.

The hydrocarbon was oxidized with potassium permanganate. 10 g

of the hydrocarbon required 37 g of $KMnO_4$. The MnO_2 precipitate was filtered out, and the neutral products were driven off with steam and extracted with ether. The ether was drawn off in vacuum, the residual oily liquid crystallizing when it was chilled with ice (according to Kizhner, the melting point of benzoyltrimethylene is 5°). The semicarbazone was prepared as beautiful lustrous white needles; b.p. 177-177.5° (from alcohol). The m.p. is 184° according to Kizhner.

0.0308 g substance: 5.5 ml N_2 (24°, 763 mm).
Found %: N 20.64.
$C_{11}H_{13}ON_3$. Computed %: N 20.69.

The solution left after the neutral products had been driven off was then placed in an extractor for two days. After the ether had been driven off, a white crystalline substance was left, which was pressed out on a porous plate. The resulting crystals had a sharp m.p. of 53°.

0.0990 g substance: 0.2708 g CO_2; 0.0694 g H_2O.
0.0883 g substance: 0.2403 g CO_2; 0.0625 g H_2O.
Found %: C 74.60, 74.22; H 7.84, 7.92.
$C_{11}H_{14}O_2$. Computed %: C 74.16; H 7.86.
0.0403 g substance: 9.32 ml CH_4 (8.5°, 776 mm).
0.0545 g substance: 16.82 ml CH_4 (12.1°, 776 mm).
Found %: active H 1.022, 1.0342; active H atoms, 1.80, 2.36.
$C_{11}H_{12}(OH)_2$. Computed %: active H 1.132; active H atoms, 2.

The substance was oxidized with lead tetraacetate by the Criege method [11]. Freshly prepared lead tetraacetate was heated for 2 hours over a water bath at 50-60° with 0.5 g of the glycol in a small flask fitted with a reflux condenser, after which the flask contents were neutralized with a potash solution and desiccated with potash. The precipitated mineral salt was filtered out, and the neutral products were driven off from the filtrate; the semicarbazone was then prepared from the neutral products. The melting point was 177° after double recrystallization from alcohol. A test sample mixed with benzoyltrimethylene semicarbazone, secured by oxidizing the hydrocarbon with potassium permanganate, exhibited no depression.

Analysis of the Substance with a M.p. of 138-140° at 8 mm:

d_4^0 1.058; d_4^{22} 1.040; n_α^{22} 1.5366; MR_α 56.84.

$C_{12}H_{14}O_2F_4$. Computed: MR_α 54.81.

0.1220 g substance: 0.3385 g CO_2; 0.0833 g H_2O.
0.0890 g substance: 0.2471 g CO_2; 0.0569 g H_2O.
Found %: C 75.67, 75.72; H 7.64, 7.16.
$C_{12}H_{14}O_2$. Computed %: C 75.79; H 7.37
0.1476 g substance: 10.23 g benzene: Δt 0.39°.
Found: M 189.8
$C_{12}H_{14}O_2$. Computed: M 190.0.

5 g of the substance, dissolved in chloroform, was ozonized. The ozonide was decomposed by a soda solution while heated over a water bath. The neutral products were driven off with steam. A semicarbazone, with a m.p. of 194° (from alcohol) was prepared; it exhibited no depression when mixed with the semicarbazone of known acetophenone. The remaining solution was acidulated with sulfuric acid, and the volatile acids were driven off. The distillate was found to contain formic acid (a white calomel precipitate, which turned black when ammonia was added). We were unable to find acrylic acid in the ozonolysis products. Oxidation of the ester with potassium permanganate likewise yielded acetophenone and formic acid, which again interfered with the determination of the acrylic acid.

Saponifying the ester. 15 g of the ester was heated for 20 hours, with constant stirring, with twice the amount of a 20% potash solution, after which the upper layer was separated, washed with water and desiccated with potash, and ether extracts were made of the lower layer. After desiccation and driving off of the solvent, the residue was vacuum-distilled, yielding an unsaponified ester. The alkaline solution was acidulated with sulfuric acid, the mineral salts were filtered out, and the filtrate was steam distilled. No formic acid was found in the distillate, which again indicated that the ester was not saponified.

The recovered ester was reacted with 20% KOH to saponify it. The heating and stirring was continued for 64 hours, but was also unsuccessful.

An endeavor was made to saponify the ester by the Auwers method. 20 g of the ester, dissolved in dilute ethyl alcohol (26 g of alcohol and 12 g of water), was placed in a round-bottomed flask. The mixture was brought to a boil, and a solution of 4.2 g of NaOH in 4.2 g of water was added from a dropping funnel. It took an hour to add the alkali, and then stirring was continued for another 40 minutes. The top layer was separated and desiccated; it turned out to be the unsaponified ester, while no formic acid was found in the aqueous layer.

Decomposing the ester with ethylmagnesium bromide. 20 g of C_2H_5Br dissolved in ether was added to 3.6 g of magnesium covered with ether. Stirring was continued for another hour after all the ethyl bromide had been added. 14.7 g of 2-phenylpenten-2-ol-3 formate, dissolved in 50 ml of absolute ether, was added to the resulting ethylmagnesium bromide. The reaction is extremely violent, and the reactor had to be chilled with ice water. The organomagnesium coordination compound was decomposed with ice water and sulfuric acid (1:5). The reaction products were extracted with ether and desiccated with potash. The ether was driven off, and the residue was distilled at first under atmospheric pressure. 1.1 g of a 100-120° fraction, representing diethylcarbinol (b.p. 117°), was collected; distillation was then continued at a vacuum of 12 mm. This yielded the following fractions: 1) 0.6 g at 29-138°; and 2) 9.9 g at 138-144°. The second fraction was redistilled, yielding 8.6 g of a substance with a b.p. of 142-144° at 12 mm. The fraction representing the diethylcarbinol was sealed into an ampoule with phenyl isocyanate. The resulting phenylurethane had a m.p. of 48° after recrystallization from alcohol, which is in agreement with the figure given in the literature.

0.2117 g substance: 14 ml N_2 (24°, 763 mm).
Found %: N 7.45.
$C_{12}H_{11}O_2$. Computed %: N 6.96.

Analysis of the Alcohol 2-Phenylpenten-2-ol-5

d_4^{23} 1.032; n_α^{23} 1.5573; MR_α 50.65.

$C_{11}H_{14}OF_4$ Computed: MR_α 50.09.

0.0991 g substance: 0.2955 g CO_2; 0.0771 g H_2O.
0.1028 g substance: 0.3068 g CO_2; 0.0790 g H_2O.
Found %: C 81.33, 81.43; H 8.70, 8.60.
$C_{11}H_{14}O$. Computed %: C 81.49; H 8.64.

Hydrogenating 2-phenylpenten-2-ol-5. 5 g of the alcohol and 1 g of the catalyst – platinum black, prepared by the Wilstätter-Fokin method – were used in hydrogenation. Hydrogenation was effected in absolute alcohol and was extremely slow (taking about 10 hours). After hydrogenation was complete, the platinum black was filtered out, the alcohol was driven off, and the residue was distilled in vacuum; the substance distilled at 128-133° (11 mm). The resultant product

decolorized $KMnO_4$ very slightly. The alcohol was treated with 0.4 g of potassium permanganate to eliminate the traces of unsaturated compounds. The MnO_2 precipitate was filtered out and boiled thoroughly with ether in a flask fitted with a reflux condenser. The neutral products driven off from the aqueous solution were extracted with ether, the ether extracts were desiccated with potash, the ether was driven off, and the residue was distilled in vacuum. The resulting alcohol boiled at 132-133° (11 mm):

d_4^{20} 0.9962; d_4^{20} 0.9822; n_α^{20} 1.5164; MR_α 50.43

$C_{11}H_{16}O$. Computed: MR_α 50.59.

Oxidizing γ-phenyl amyl alcohol with a chromic acid mixture, by the Houben method. 2 g of the alcohol was heated for 40 minutes, with a reflux condenser, with 1.88 g of $Na_2Cr_2O_7 \cdot 2H_2O$, 24 ml of water, and 2.5 g of sulfuric acid. The solution turned green. After it had cooled, the solution was extracted with ether, the ether extracts likewise being green; the color of the ethereal solution persisted even after it had been washed with water. The solution was desiccated with calcined sodium sulfate, the ether driven off, and the dark-green mass remaining as a residue was not distilled in vacuum (according to the literature, γ-phenylvaleric acid boils at 170° and 10 mm). Dilute (1:5) sulfuric acid was added to eliminate inorganic impurities. When we tried to distil the γ-phenylvaleric acid with steam, yellow drops of an oil floated to the surface in the distilling flask; they did not distil with steam and were extracted with ether. After the ether had been removed, a thick yellow mass was left, which had an acid reaction. The resulting acid was dissolved in hot ammonia, and the excess ammonia was eliminated by boiling. A concentrated solution of $AgNO_3$ was added to the resultant solution. The precipitated silver salt was analyzed.

0.0551 g substance: 0.0209 g Ag.
0.0492 g substance: 0.0187 g Ag.
Found %: Ag 37.93, 38.00.
$C_{11}H_{13}O_2Ag$. Computed %: Ag 37.89.

II. Reaction of Methylphenylallylcarbinol With Formic Acid

Synthesis of methylphenylallylcarbinol. The methylphenylallylcarbinol was produced by the method developed by Sh. A. Fridman [10]. Some methyl or ethyl iodide was added to 12 g of magnesium, covered with a small amount of ether, in order to induce the reaction. Then a solution of 65 g of acetophenone, 64 g of allyl bromide in 200 g of an ether-benzene mixture (1:1 by weight) was added drop by drop. The reaction was carried out while heating to 45° over a water bath. It took 5 hours to add the above solution, and then the reaction mixture was stirred for another 2½ hours at the same temperature. The next day the organomagnesium coordination compound was decomposed with ice water and sulfuric acid (1:5). The ether-benzene layer was separated, and ether extracts made of the aqueous layer. After the extracts had been desiccated with potash and the solvent had been driven off, the residue was distilled in vacuum. The unreacted acetophenone (25-27%) distilled at first, followed by the synthesized alcohol. Redistillation yielded 34 g of an alcohol with a b.p. of 99-101° at 9 mm, or 51%, based on the acetophenone that entered into the reaction.

Reaction of methylphenylallylcarbinol with 80% formic acid. 30 g of methylphenylallylcarbinol was heated for an hour and a half, with a reflux condenser, with 90 g of 80% formic acid, after which the top layer was separated, washed with a soda solution and with water, and desiccated with calcined potash. Ether extracts were made from the bottom layer, which had been neutralized with anhydrous soda, and the extracts were desiccated with calcined potash. An endeavor

was made to distil the resultant product at 10 mm, but without success. The polymer, poured into a crystallizer, solidified into a transparent, light-yellow mass.

0.1082 g substance: 0.3622 g CO_2; 0.0792 g H_2O.
0.1084 g substance: 0.3639 g CO_2; 0.0818 g H_2O.
Found %: C 91.30, 91.47; H 8.18, 8.44.
$C_{11}H_{12}$. Computed %: C 91.67; H 8.33.

Reaction of methylphenylallylcarbinol with 48% formic acid. 30 g of the alcohol was added to 90 g of 48% formic acid. The reaction lasted 3 hours at room temperature, with constant stirring. After the reaction was over, the top layer was separated, washed with soda and then with water, and ether extracts were made of the neutralized bottom layer. After desiccation and after the ether had been driven off, the residue was distilled in vacuum, two fractions being collected: 1) 89-97° at 9 mm – 9.5 g (31.7%); and 2) 97-101° at 9 mm – 18 g (60.0%). The first fraction was redistilled, yielding about 7 g of a hydrocarbon with a b.p. of 88-90° at 13 mm. The second fraction was the alcohol that had not reacted.

Analysis of the Hydrocarbon with a b.p. of 88-90° at 13 mm:

d_4^0 0.9668; d_4^{23} 0.9472; n_α^{23} 1.5429; MR_α 47.86.

$C_{11}H_{12}F_5$. Computed: MR_α 48.07.

0.1468 g substance: 0.4928 g CO_2; 0.1074 g H_2O.
0.0780 g substance: 0.2616 g CO_2; 0.0585 g H_2O.
Found %: C 91.55, 91.46; H 8.19, 8.39.
$C_{11}H_{12}$. Computed %: C 91.67; H 8.33.

0.1556 g substance; 17.15 g benzene: Δt 0.32°.
Found: M 145.4
$C_{11}H_{12}$. Computed: M 144.

Another test was run with acid of the same concentration, but with boiling the mixture for one hour and a half. The hydrocarbon yield was 54% in this test.

Oxidizing the hydrocarbon. 4.6 g of the hydrocarbon required 32 g of potassium permanganate. The neutral products yielded a negligible quantity of acetophenone, recovered as its semicarbazone with a m.p. of 194° (from alcohol), which exhibited no depression when mixed in a test sample with the semicarbazone of known acetophenone. The salt solution was evaporated, acidulated, and extracted with ether. The extracts were desiccated with sodium sulfate, and the ether was driven off; this yielded benzoic acid, which fused at 121° after double sublimation and exhibited no depression when mixed in a test sample with known benzoic acid. Oxalic acid was recovered as its calcium salt, desiccated at 100° to constant weight, from the solution left after the benzoic acid had been extracted.

0.1296 g substance: 0.0569 g CaO.
0.1023 g substance: 0.0450 g CaO.
Found %: CaO 43.88, 43.98.
C_2O_4Ca. Computed %: CaO 43.75.

Reaction of methylphenylallylcarbinol with 98% formic acid. 40 g of 98% formic acid was added to 30 g of the alcohol. The reaction was carried out for three hours, with constant stirring and chilling with ice. Some water was added to the flask after the reaction was over; the upper layer that formed was separated, washed with soda and with water, and desiccated with calcined potash. Ether extracts were made of the neutralized lower layer. After desiccation and after the ether had been driven off, the residue was distilled in vacuum, yielding 35% of a fraction representing the hydrocarbon 2-phenylpentadiene-1,4 and 25% (7.5 g) of a fraction with a b.p. of 108-114° at 10 mm. Some 2 g of a polymer remained in the distilling flask. Redistillation of the 108-114° (10 mm) fraction yielded

5 g of a substance with a b.p. of 112-114° at 10 mm, the constants and analysis of which indicated that it was the ester of methylphenylallylcarbinol and formic acid.

0.1222 g substance: 0.3401 g CO_2; 0.0798 g H_2O.
0.1023 g substance: 0.2853 g CO_2; 0.0686 g H_2O.
Found %: C 75.82, 76.05; H 7.31, 7.50.
$C_{12}H_{14}O$. Computed %: C 75.79, H 7.37.

d_4^{20} 1.0397; d_4^{20} 1.0105; n_α^{20} 1.5179; MR_α 56.85.

$C_{12}H_{14}O_2F_4$. Computed: MR_α 54.81.
0.1482 g substance; 16.84 g benzene: Δt 0.24°.
Found: M 188.
$C_{12}H_{14}O_2$. Computed: M 190.

Saponifying the ester of methylphenylallylcarbinol. 8.5 g of the ester was brought to a boil with a solution of 6 g of K_2CO_3 in 24 ml of water for 27 hours with constant stirring. After heating was over, the upper layer was separated, washed with water, and desiccated with calcined potash. Ether extracts were made of the lower layer. The extracts were desiccated, the ether was driven off, and the residue was distilled in vacuum. This yielded 6.7 g of a fraction with a b.p. of 98-103° at 10 mm. The boiling point indicated that the substance recovered was methylphenylallylcarbinol. To prove that it contained no traces of the cyclic alcohol, which might have been formed during the saponification of the ester, the synthesized alcohol was oxidized with potassium permanganate, but no neutral products were recovered, except for negligible traces of acetophenone; the only product of the ester's saponification thus proved to be methylphenylallylcarbinol.

III. The Reaction of Methylethylcyclopropylcarbinol With Formic Acid

(By the student S. E. Chernobelskaya)

50 g of acetyltrimethylene was added drop by drop, while chilled by ice, to ethylmagnesium bromide, prepared from 14 g of magnesium and 65 g of ethyl bromide. The resultant organomagnesium coordination compound was decomposed with ice water and dilute sulfuric acid. The reaction products were extracted with ether, desiccated with calcined potash, and distilled. Repeated distillations yielded 21.5 g of a substance with a b.p. of 141-142°, or 42%. The resulting methylethylcyclopropylcarbinol did not decolorize a $KMnO_4$ solution and possessed the following constants:

d_4^{20} 0.8869; n_α^{20} 1.4396; MR_α 33.84.

$C_7H_{14}O$. Computed: MR_α 33.70.

Action of formic acid on methylethylcyclopropylcarbinol. 30 g of methylethylcyclopropylcarbinol was heated to a boil for two hours with 90 g of 80% formic acid. After cooling, the reaction products were diluted with water, and the liquid separated into layers. The upper layer was removed, washed with soda solution and with water, and desiccated with calcined potash. Ether extracts were made of the lower layer. Driving off the ether and distilling the residue yielded 14 g of a substance with a b.p. of 119-121°.

Analysis of the Substance with a b.p. of 119-121°:

0.2054 g substance: 0.5569 g CO_2; 0.2261 g H_2O.
0.1625 g substance: 0.4399 g CO_2; 0.1864 g H_2O.
Found %: C 73.94, 73.83; H 12.31, 12.43.
$C_7H_{14}O$. Computed %: C 73.68; H 12.28.

The substance with a b.p. of 119-121° slowly decolorizes a $KMnO_4$ solution and exhibits no reaction for a hydroxyl or carbonyl group.

Oxidizing the substance with a b.p. of 119-121°. 14.8 g of the substance with a b.p. of 119-121° was first oxidized with a 1% $KMnO_4$ solution, and then the pulverized anhydrous salt was poured into the bottle in which oxidation was being effected. Oxidation was extremely slow at room temperature, lasting 3 hours. Permanent coloration appeared after 32 g of $KMnO_4$ had been added. No neutral products were produced by oxidation. After a concentrated solution of the salt had been acidulated with sulfuric acid, an oily layer floated at the surface of the solution. Ether extracts were made of the aqueous solution. The resultant product boiled at 218-222° at atmospheric pressure after it had been desiccated with calcined sodium sulfate. Analysis of this substance indicated that it was the lactone of γ-methyl-γ-hydroxycaproic acid. Refractinnation yielded 10 g of a substance with a b.p. of 220-221°; the yield was 60%.

Analysis of the Substance with a b.p. of 220-221°:

d_4^0 1.0191; d_4^{18} 1.0025; d_4^{20} 1.0009; n_α^{18} 1.4401; MR_α 33.66.
$C_7H_{12}O_2$. Computed: MR_α 33.82.

0.1554 g substance: 0.3755 g CO_2; 0.1322 g H_2O.
0.1585 g substance: 0.3825 g CO_2; 0.1346 g H_2O.
Found %: 65.90, 65.82; H 9.52, 9.50.
$C_7H_{12}O_2$. Computed %: C 65.63; H 9.37.

0.1581 g substance: 15.07 g benzene: Δt 0.415°.
Found: M 126.3.
$C_7H_{12}O_2$. Computed: M 128.

The lactone was boiled with an excess of alkali until it dissolved completely in order to determine its neutralization equivalent. The excess alkali was titrated back with acid.

Found: M 126.7, 127.
$C_7H_{12}O_2$. Computed: M 128.

To secure the silver salt, the lactone was dissolved in ammonia by heating it over a water bath in a beaker covered with a watch glass. The resultant ammonium salt was treated with $AgNO_3$ after the excess ammonia had been driven off by evaporation. The snow-white silver salt that settled out was analyzed.

0.0723 g substance: 0.0312 g Ag.
0.0603 g substance: 0.0253 g Ag.
Found %: Ag 42.91, 42.79.
$C_7H_{13}O_3Ag$. Computed %: Ag 42.69.

Synthesizing the lactone's amide by Fittig's method [12]. When the lactone was treated in the cold with a concentrated solution (25%) of ammonia, with frequent agitation, the lactone entered into solution very slowly. The crystals that settled out when this solution was evaporated in vacuum over sulfuric acid were pressed out on a porous plate; their m.p. was 94-95°. The resulting γ-methyl-γ-hydroxycaproamide dissolved very readily in water and alcohol, while it was hardly soluble at all in ether.

0.0786 g substance: 6.45 ml N_2 (19°, 769 mm).
Found %: N 9.56.
$C_7H_{13}O_2N$. Computed %: N 9.65.

SUMMARY

1. A study has been made of the action of formic acid on methylphenylcyclopropylcarbinol, methylethylcyclopropylcarbinol, and methylphenylallylcarbinol.

2. It has been shown that when methylphenylcyclopropylcarbinol is heated with formic acid, a hydrocarbon, asymmetrical phenylcyclopropylethylene, and an ester of the unsaturated primary alcohol 2-phenylpenten-2-ol-5 are formed.

3. It has been proved that this involves the isomerization of the three-membered ring to an open chain, and the mechanism of this isomeric transformation has been put forward.

4. In view of the fact that the ester of 2-phenylpenten-2-ol-5 could not be saponified by the methods employed, it was decomposed by reacting it with ethylmagnesium bromide. The structure of the resulting alcohol, 2-phenylpenten-2-ol-5 was demonstrated by hydrogenating it to γ-phenyl amyl alcohol, followed by its oxidation to γ-phenylvaleric acid.

5. It has been shown that when methylphenylallylcarbinol is heated with formic acid of various concentrations, a mixture of hydrocarbons with isolated and conjugated double bonds results: 2-phenylpentadiene-1,4 and 4-phenylpentadiene-1,3.

6. The action of concentrated formic acid at 0° results in the formation, in addition to the hydrocarbons, of an ester of methylphenylallylcarbinol, which yields the original unsaturated alcohol upon saponification. Thus no isomeric transformation, with formation of a cyclic alcohol, takes place in this case.

7. It has been shown that when methylethylcyclopropylcarbinol is heated with formic acid, this alcohol is isomerized to the gamma oxide of 1-methyl-1-ethyltetramethylene or 4-methyl-4-ethyltetrahydrofuran.

8. The structure of the oxide has been proved by oxidizing it to a lactone of γ-methyl-γ-hydroxycaproic acid.

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THE SYNTHESIS OF HYDROCARBONS

XII. THE HYDROBROMIDES OF DIENE HYDROCARBONS IN THE SYNTHESIS OF OLEFIN AND PARAFFIN HYDROCARBONS WITH A QUATERNARY CARBON ATOM

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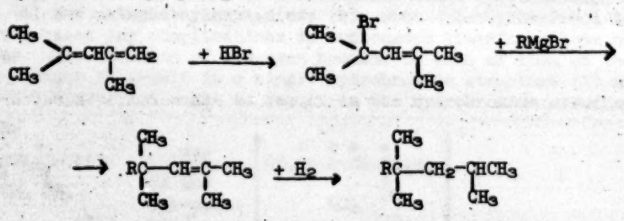
N. D. Zelinsky Laboratory of Organic Chemistry, Moscow State University, awarded the Order of Lenin

In our previous papers [1,2,3,4] we described the reaction of 2,4-dimethyl-1,3-pentadiene hydrobromide with organomagnesium compounds.

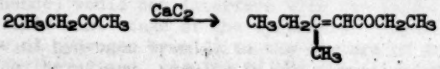
This reaction was a new preparative method for synthesizing hydrocarbons with a quaternary carbon atom – the 2,4,4-trimethylalkenes – and from them the 2,4,4-trimethylalkanes (by hydrogenation).



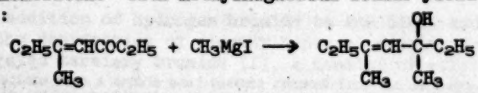
Thus the initial substance in this synthesis was a diene hydrocarbon with conjugated double bonds – 2,4-dimethyl-1,3-pentadiene, which can be readily synthesized by reacting mesityl oxide with methylmagnesium iodide.

We thought it important and interesting to endeavor to use this new method of synthesizing hydrocarbons with a quaternary carbon atom for a wider range of diene hydrocarbons with conjugated double bonds, resembling 2,4-dimethyl-1,3-pentadiene in their structure, i.e., yielding tertiary bromides, homologs of allyl bromide, when reacted with one molecule of hydrogen bromide.

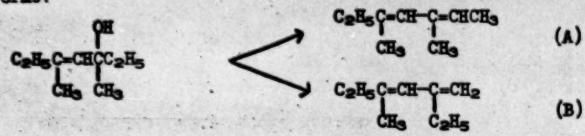
In the present research we used as our initial substance an α,β-unsaturated ketone, a "homomesitone," a homolog of mesityl oxide, formed by condensing two molecules of methyl ethyl ketone by having alkaline condensing agents act upon them [5]; the structure of this ketone has been determined by many authors [6]:



Reacting the "homomesitone" with methylmagnesium iodide yielded an unsaturated tertiary alcohol:



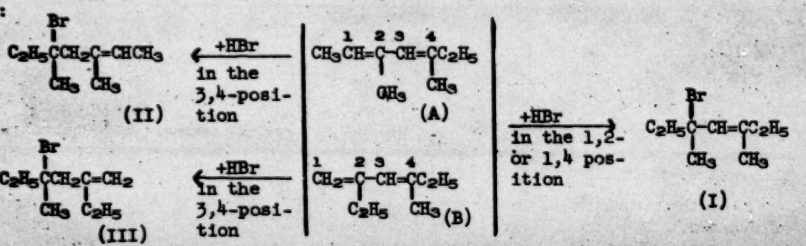
Dehydration of the resultant dimethylheptenol might lead to the formation of a mixture of two conjugated* diene hydrocarbons – 3,5-dimethyl-2,4-heptadiene (A) and 4-methyl-2-ethyl-1,3-hexadiene (B), which may exist in several stereoisomeric forms:



Actually, it was found that dehydration of the dimethylheptenol results in formation of a mixture of diene hydrocarbons, which distils (above sodium) into a tower throughout a wide temperature range (136-142°).

In subsequent tests the dimethylheptenol was not recovered in its individual state; the product of the reaction between methylmagnesium iodide and the "homomesitone" was heated for several hours (after the ether had been driven off), and the resulting mixture of diene hydrocarbons was slowly distilled. The yield of the hydrocarbon fraction was 86% of the theoretical yield (based on the initial "homomesitone"). Thus the "homomesitone" like its lower homolog – mesityl oxide and in contrast to the other α,β-unsaturated ketones [7], reacts normally with an organomagnesium compound at its carbonyl group, giving rise to a readily dehydrated unsaturated tertiary alcohol.

The formation of a mixture of two isomeric diene hydrocarbons, dimethylheptadiene (A) and methylethylheptadiene (B), when dimethylheptenol is dehydrated could not cause any complications in subsequent transformations of these hydrocarbons. The addition of hydrogen bromide to each of them at the 1,2- and 1,4-position ought to result in a single hydrobromide structure (I) and its addition at the 3,4-position ought to result in the hydrobromide structure (II) or (III):

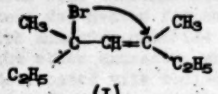


Of the three possible products of the hydrobromination reaction, the bromides of structure (II) or (III) are not homologs of allyl bromide, and the mobility of their halogen atom ought to be much less than in the bromide of structure (I), which is an unsaturated tertiary bromide that is a homolog of allyl bromide. It might therefore be supposed that even if both bromides (II) and (III) were formed, they would not react under ordinary conditions with organomagnesium compounds and, hence, would not interfere with the production of the individual hydrocarbons in this next stage of the synthesis. Experiment has shown that adding one molecule of hydrogen bromide to the mixture of dimethylheptadiene and its isomer, methylethylhexadiene, results in the formation of only one hydrobromide, which boils within half a degree and reacts violently with a Grignard reagent.

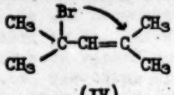
Thus, the addition of hydrogen bromide to the diene hydrocarbon that is the product of the dehydration of dimethylheptenol results in the formation of only the unsaturated tertiary bromide (I), a homolog of allyl bromide, which can

*Inasmuch as a homomesitone with a double bond further removed from the carbonyl group [6] may be formed when methyl ethyl ketone is condensed with the aid of calcium carbide, the resultant hydrocarbon mixture might contain as an impurity of diene hydrocarbons an isolated type with the same carbon skeleton.

exist in only one form because of the peculiarity of its structure, which excludes the possibility of allyl rearrangement (inasmuch as the first and third carbon atoms in the three-carbon allyl system of this bromide are attached to identical radicals):



(I)



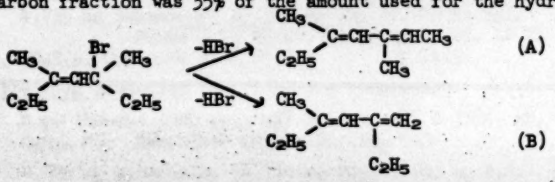
(IV)

The 2,4-dimethylpentadiene hydrobromide previously studied by us [1], whose reaction with organomagnesium compounds resulted in the formation of hydrocarbons with a quaternary carbon atom, possessed a structure of a similar type (IV)

The tertiary unsaturated bromide synthesized in the present research, 5-bromo-3,5-dimethyl-3-heptene (α,γ-dimethyl-α,γ-diethylallyl bromide), was then reacted with organomagnesium compounds. The products of this reaction turned out to be ethylenic hydrocarbons (the yield was about 30% of the theoretical, based on the mixture of alkadienes used for the hydrobromination reaction), formed by the substitution of the radical in the organomagnesium compound for the bromine atom in the hydrobromide (I):

The presence of a quaternary carbon atom in the synthesized alkenes was demonstrated by analyzing the oxidation products of one of these alkenes, as well as by analyzing the Raman spectra of the corresponding alkenes.

A by-product in the reaction of the hydrobromide with organomagnesium compounds proved to be the original mixture of diene hydrocarbons (136-142°) formed as the result of detaching hydrogen bromide from the hydrobromide (I); the yield of this hydrocarbon fraction was 35% of the amount used for the hydrobromination reaction:



(A)

(B)

EXPERIMENTAL

The 3-methyl-3-hepten-5-one (the "homomesitone") was synthesized by reacting methyl ethyl ketone with calcium carbide in a Soxhlet apparatus [8]. The methyl ethyl ketone that did not enter into the reaction was driven off, and the residue was distilled into a tower with an efficiency of 25 theoretical trays. The resulting 3-methyl-3-hepten-5-one (with a possible trace of 3-methyl-2-hepten-5-one) had the following constants:

Bp. 165-167° (760 mm); n_D^{20} 1.4476; d_4^{20} 0.8560; MR_D 39.44.
$C_8H_{14}O$ F. Computed: MR_D 38.86; EM_D 0.58.

Literature data: B.p. 64-70° (20 mm); $n_D^{21.4}$ 1.4450; d_4^{21} 0.8565 [8];
B.p. 164-165° (760 mm); n_D^{18} 1.4491; d_4^{25} 0.853 [8].

Reaction of "homomesitone" with methylmagnesium iodide. An ethereal solution of "homomesitone" (the molar proportions of the ketone, the methyl iodide, and the magnesium were 1:1.5:1.5, respectively) was added to an ethereal solution of methylmagnesium iodide with constant stirring and chilling (with snow and salt). Then the reaction mixture was heated for seven hours and decomposed by pouring it over ice, after which ammonium chloride was added to it. After the ether had been driven off from the ether extracts, which had been washed until their reaction was neutral and desiccated with sodium sulfate, the diene hydrocarbons were driven off with the water formed during the dehydration of the tertiary alcohol, which had the following constants:

B.p. 176-177° (750 mm); n_D^{20} 1.4525; d_4^{20} 0.8531; MR_D 45.01.
$C_9H_{18}O$. Computed: MR_D 44.93.

5.145 mg substance: 14.325 mg CO_2; 6.090 mg H_2O.
3.950 mg substance: 11.000 mg CO_2; 4.625 mg H_2O.
Found %: C 75.96, 75.95; H 13.25, 13.10.
$C_9H_{18}O$. Computed %: C 75.97; H 12.75.

The tertiary alcohol was not recovered in our subsequent experiments. To complete the dehydration, the product of the reaction between the "homomesitone" and the methylmagnesium iodide was heated for three hours after the ether had been driven off and then slowly distilled. The resulting hydrocarbon layer was separated from the aqueous layer, desiccated with calcium chloride, and fractionated over sodium into a tower with 25 theoretical trays. A diene fraction with a b.p. of 136-142° (760 mm) was collected, its yield being 86% of the theoretical, based on the original unsaturated ketone. The 75 g of this 136-142° fraction yielded two major fractions after fractionation above sodium into a tower: 36 g with a b.p. of 137-138° (760 mm), and 24 g with a b.p. of 140-141°.

The first fraction possessed the following constants:

B.p. 137-138° (760 mm); n_D^{20} 1.4487; d_4^{20} 0.7660; MR_D 43.42.
C_9H_{16} F 2. Computed: MR_D 42.82; EM_D 0.6.

5.510 mg substance: 17.628 mg CO_2; 6.242 mg H_2O.
4.735 mg substance: 15.152 mg CO_2; 5.400 mg H_2O.
Found %: C 87.26, 87.27; H 12.68, 12.76.
C_9H_{16}. Computed %: C 87.09; H 12.91.

The second fraction possessed the following constants:

B.p. 140-141 (760 mm); n_D^{20} 1.4502; d_4^{20} 0.7684; MR_D 43.63.
C_9H_{16} F 2. Computed: MR_D 42.82; EM_D 0.8.

4.670 mg substance: 14.770 mg CO_2; 5.699 mg H_2O.
4.055 mg substance: 12.825 mg CO_2; 4.485 mg H_2O.
Found %: C 86.98, 86.80; H 13.02, 13.20.
C_9H_{16}. Computed %: C 87.09; H 12.91.

By analogy with the diene hydrocarbons synthesized by Jacquemain [9] in a similar manner (reacting mesityl oxide with organomagnesium compounds), we may assume that the fraction with the lower constants consists largely of dimethylheptadiene (A), while the fraction with the higher constants consists of methylethylhexadiene (B). Neither 3,5-dimethyl-2,4-heptadiene nor 4-methyl-2-ethyl-1,3-hexadiene is described in the literature.

Our endeavors to obtain addition products of the synthesized diene hydrocarbons and maleic anhydride (in a toluene or benzene solution) were unsuccessful.

Addition of hydrogen bromide to the synthesized diene hydrocarbons. A current of anhydrous hydrogen bromide was passed through the mixture of diene hydro-

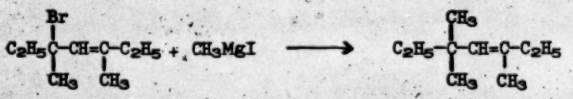
carbons (136-142°; 10 g), chilled with snow and salt, until the increase in weight* corresponded to the addition of one molecule of hydrogen bromide (6-6.5 g). The resulting hydrobromide (5-bromo-3,5-dimethyl-3-heptene) was distilled in vacuum; its constants were as follows:

B.p. 63-63.5° (7 mm); n_D^{20} 1.4704; d_4^{20} 1.1210; MR_D 50.90.

$C_9H_{17}Br$ ⌈. Computed: MR_D 51.06.

The hydrobromide turns yellow upon standing. Adding hydrogen bromide to each of the two narrow fractions of diene hydrocarbons (137-138° and 140-141°) resulted in the formation of a hydrobromide with the same constants. The hydrobromide (I) was not distilled in subsequent experiments, but was dissolved in absolute ether as soon as it was produced and then reacted with organomagnesium compounds.

Reaction of 5-Bromo-3,5-dimethyl-3-heptene with Methylmagnesium Iodide



48 g of the hydrobromide, dissolved in ether and chilled to -40 to -50°, was added during the course of half an hour to an ether solution of methylmagnesium iodide (50 g of methyl iodide and 8.2 g of magnesium), with constant stirring and chilling to the same temperature. The reaction mixture was then stirred for another 2 hours while chilled (to -40°) and for 5 hours the next day while heated. Decomposition was effected by pouring the reaction mixture over ice and then adding ammonium chloride. After the ether had been driven off from the ether extracts, which had been washed and then desiccated with calcium chloride, the residue was fractionated over sodium (into a tower with 25 theoretical trays). The resulting hydrocarbon, 3,5,5-trimethyl-3-heptene (12.7 g, 31% of the theoretical), possessed the following constants:

B.p. 151-152° (764 mm); n_D^{20} 1.4350; d_4^{20} 0.7638; MR_D 47.91.

$C_{10}H_{20}$ ⌈. Computed: MR_D 47.91.

I.L.Kondakov [10] condensed asymmetrical methylethylethylene with tertiary amyl chloride and synthesized a hydrocarbon (b.p. 157-157.5 at 759 mm; d_4^{20} 0.7729), to which he ascribed the structure of 3,5,5-trimethylheptene-3.

Fractionation of the reaction product again yielded the original mixture of diene hydrocarbons (10 g; 35% by weight of the hydrocarbons used in the hydrobromination reaction) with a b.p. of 137-141°; n_D^{20} 1.4480; d_4^{20} 0.7650, which was formed as the result of the detaching of hydrogen bromide from the tertiary alcohol during the reaction.

Oxidizing 3,5,5-trimethyl-3-heptene. 14 g of potassium permanganate was added in the course of 24 hours, with constant stirring, to a solution of 5 g of 3,5,5-trimethyl-3-heptene in 100 ml of acetone (treated preliminarily by heating it with potassium permanganate). The usual treatment yielded 1.5 g of dimethylethylacetic acid with a b.p. of 186-187°; its p-phenylphenacyl ester had a m.p. of 83°.

Analysis of the p-Phenylphenacyl Ester:

4.885 mg substance: 13.788 mg CO_2; 3.210 mg H_2O.
5.825 mg substance: 16.439 mg CO_2; 3.873 mg H_2O.
Found %: C 76.99, 76.97; H 7.35, 7.44.
$C_{20}H_{22}O_3$. Computed %: C 77.41; H 7.09.

Literature data on dimethylethylacetic acid: A.E.Favorsky [11] – b.p.

*The reaction vessel was balanced on the scales the reaction lasted 40 minutes.

186-187°; Drake and Bronitsky [12] – m.p. of the phenylphenacyl ester = 86°.

Catalytic hydrogenation of 3,5,5-trimethyl-3-heptene. The hydrocarbon was passed over nickel on alumina at 160-170° in a current of hydrogen at the rate of 0.1 ml per minute. After receiving the usual treatment, the catalyzate was distilled over sodium into a tower with 25 theoretical trays. The resulting 3,3,5-trimethylheptane had the following constants:

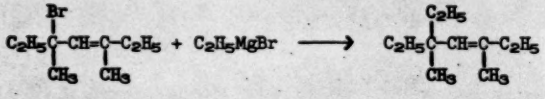
B.p. 153.5-153.7° (750 mm); n_D^{20} 1.4176; d_4^{20} 0.7440; MR_D 48.21.
$C_{10}H_{22}$. Computed: MR_D 48.38.

2.870 mg substance: 8.892 mg CO_2; 3.995 mg H_2O.
4.950 mg substance: 15.322 mg CO_2; 6.865 mg H_2O.
Found %: C 84.50, 84.42; H 15.57, 15.51.
$C_{10}H_{22}$. Computed %: C 84.73; H 15.27.

The Raman spectrum [18] of 3,3,5-trimethylheptane disclosed a frequency of 1227 (1.5), typical, according to Stepanov [13], of hydrocarbons with a quaternary carbon atom, which is in good agreement with the values of the wholly symmetrical frequencies 718 (4.5) and 730 (8) present in the spectrum.

Literature data: Drake and Welsh [14] have described the conversion of methylisopropylcarbinol by the action of sulfuric acid upon a mixture of olefin hydrocarbons, hydrogenation and fractionation of which resulted in the recovery of a paraffin hydrocarbon with a b.p. of 159.2° (767 mm); n_D^{20} 1.4208; d_4^{20} 0.7516. Johnson [15], using tertiary amyl alcohol as the original alcohol and the same series of reactions, recovered a paraffin hydrocarbon with a b.p. of 156.8°; n_D^{20} 1.4178 and d_4^{20} 0.7450. The authors attributed the structure of 3,3,5-trimethylpentane to these hydrocarbons.

Reaction of 5-Bromo-3,5-dimethyl-3-heptene with Ethylmagnesium Bromide



The reaction of 5-bromo-3,5-dimethyl-3-heptene with ethylmagnesium bromide was carried out in the same manner as described above. It produced 3,5-dimethyl-5-ethyl-3-heptene (31% of the theoretical yield), possessing the following constants:

B.p. 173-173.3° (740 mm); n_D^{20} 1.4408; d_4^{20} 0.7771; MR_D 52.45.
$C_{11}H_{22}$. Computed: MR_D 52.53.

5.095 mg substance: 15.957 mg CO_2; 6.580 mg H_2O.
4.488 mg substance: 14.055 mg CO_2; 5.810 mg H_2O.
Found %: C 85.43, 85.44; H 14.45, 14.46.
$C_{11}H_{22}$. Computed %: C 85.60; H 14.40.

3,5-Dimethyl-5-ethyl-3-heptene has not been described in the literature. The original mixture of diene hydrocarbons (35% by weight of the quantity of these hydrocarbons used for the hydrobromination reaction) was a by-product of the reaction.

Catalytic hydrogenation of 3,5-dimethyl-5-ethyl-3-heptene. Hydrogenation of the synthesized alkene over nickel on alumina (under the conditions described above) resulted in synthesis of 3,5-dimethyl-3-ethylheptane, not previously described in the literature, which possessed the following constants:

B.p. 179-179.5° (748 mm); n_D^{20} 1.4283; d_4^{20} 0.7628; MR_D 52.83.
$C_{11}H_{24}$. Computed: MR_D 53.0.

5.670 mg substance: 17.550 mg CO_2; 7.870 mg H_2O.
6.183 mg substance: 19.145 mg CO_2; 8.565 mg H_2O.
Found %: C 84.42, 84.43; H 15.53, 15.50.
$C_{11}H_{24}$. Computed %: C 84.61; H 15.39.

The Raman spectrum [16] of 3,5-dimethyl-3-ethylheptane exhibited the frequencies 1213 (2) and 1241 (1), indicating (according to Stepanov [13]) the presence of a quaternary carbon atom in the hydrocarbon's molecule, which is in good agreement with the value of the wholly symmetrical frequency 702 (10) present in the spectrum.

SUMMARY

1. The addition of one molecule of hydrogen bromide to a mixture of 3,5-dimethyl-2,4-heptadiene and its isomer, 4-methyl-2-ethyl-1,3-hexadiene, results in the formation of an unsaturated tertiary bromide, a homolog of allyl bromide, whose structure renders an allyl rearrangement impossible.

2. The reaction of this unsaturated tertiary bromide (5-bromo-3,5-dimethyl-3-heptene) with organomagnesium compounds may be used as a method of synthesizing little-known olefin hydrocarbons, and from them paraffin hydrocarbons, with a quaternary carbon atom: 3,5-dimethyl-5-ethyl-3-alkenes and 3,5-dimethyl-3-ethyl-alkanes.

3. The synthesis of several hydrocarbons of this series has been described for the first time: 3,5,5-trimethyl-3-heptene; 3,3,5-trimethylheptane; 3,5-dimethyl-5-ethyl-3-heptene; and 3,5-dimethyl-3-ethylheptane.

4. The presence of a quaternary carbon atom in these hydrocarbons was demonstrated by oxidizing one of the alkenes and analyzing the Raman spectrum of both of the alkanes.

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DERIVATIVES OF ACETYLENE

110. SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO THE STEROIDS.

VII. COMPLETE SYNTHESIS OF THE ISOMER OF 15-METHYLANDROSTENONE WITH A METHYLCYCLOPENTANE B RING

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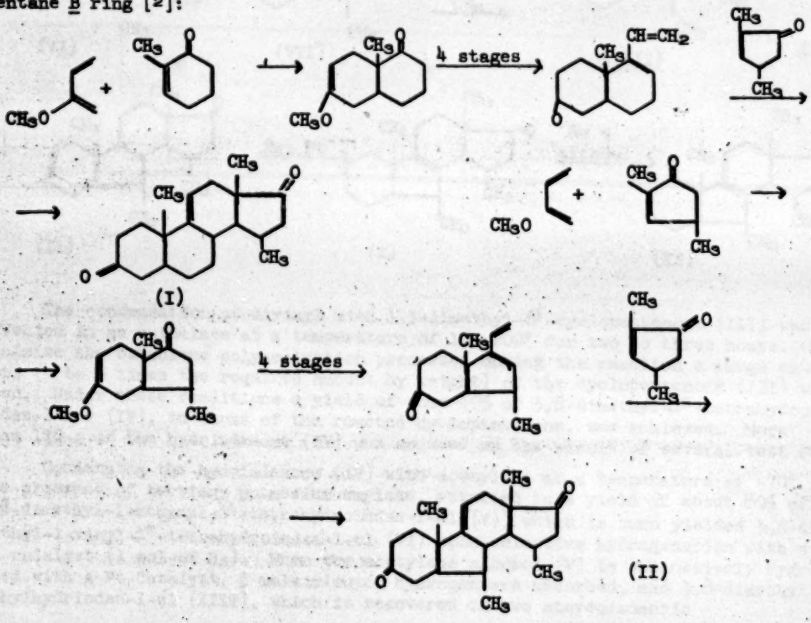
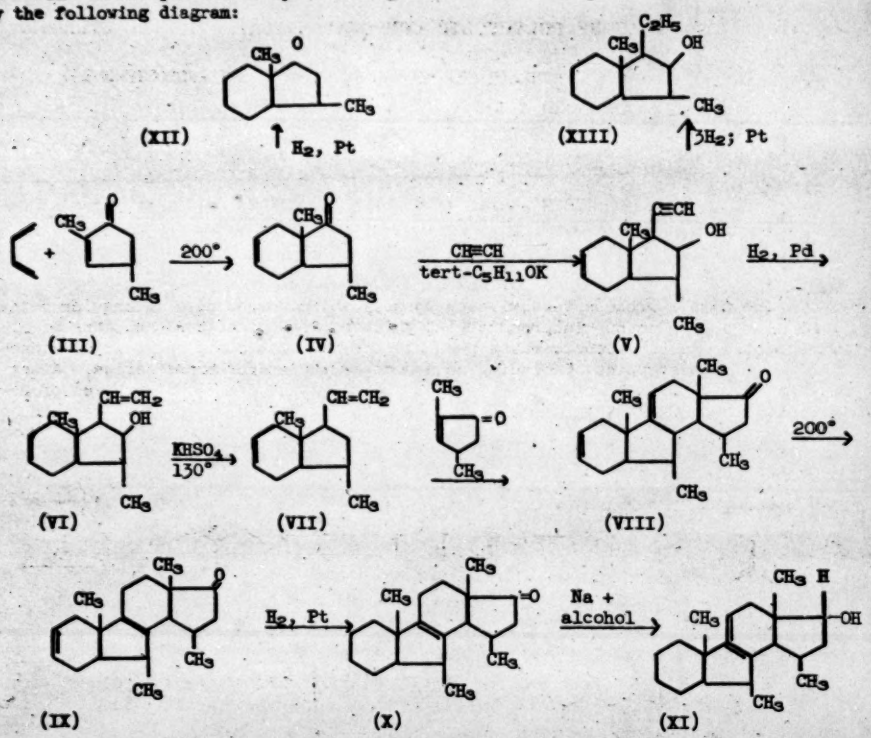
Institute of Organic Chemistry, USSR Academy of Sciences

The simple process for building up polycyclic compounds with angular methyl groups developed in our laboratory [1], which employs diene condensations of α,β-unsaturated cyclic ketones, makes possible the systematic synthesis of substances related to the steroids, including compounds of the androsterone series. After detailed investigation of the conditions governing the diene condensation of Δ^1-cyclohexenones and Δ^1-cyclopentenones with the simplest dienes by this method, our laboratory was the first to effect the complete synthesis of the stereoisomer 15-methylandrostenone (I) and of its structural isomer (II) with a methylcyclopentane B ring [2]:



The present paper describes the complete synthesis of the tetracyclic steroid ketones (IX) and (X), and of the steroid alcohol (XI), which belong to the B-norandrostane series and are isomers of the corresponding compounds of the androstane series with a methylcyclopentane B ring.

The entire process of synthesizing these steroid compounds is illustrated by the following diagram:

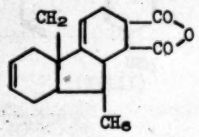


The condensation of divinyl with 1,3-dimethyl-Δ^1-cyclopentenone (III) was effected in an autoclave at a temperature of 195-200° for two to three hours. To minimize the butadiene polymerization processes during the reaction a large excess (4 to 6 times the required amount by weight) of the cyclopentenone (III) was used. Under these conditions a yield of some 40% of 3,8-dimethyl-Δ^3-tetrahydroindan-1-one (IV), in terms of the reacted cyclopentenone, was achieved. More than 170 g of the hydrindanone (IV) was secured as the result of several test runs.

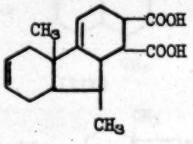
Condensing the hydrindanone (IV) with acetylene at a temperature of -70° in the presence of tertiary potassium amylate, resulted in a yield of about 80% of 3,8-dimethyl-1-ethynyl-Δ^5-tetrahydroindan-1-ol (V), which in turn yielded 3,8-dimethyl-1-vinyl-Δ^5-tetrahydroindan-1-ol (VI) upon selective hydrogenation with a Pd catalyst (1 mol of H_2). When the acetylene alcohol (V) is exhaustively hydrogenated with a Pt Catalyst, 3 molecules of hydrogen are absorbed, and 3,8-dimethyl-1-ethylhydrindan-1-ol (XIII), which is recovered in two stereoisomeric

forms (liquid and crystalline), is produced. Apparently, the acetylene and vinyl alcohols (V and VI) are also produced in the form of two liquid stereoisomers, which cannot be separated by fractionation. When the hydrindanone (IV) is hydrogenated with a Pd catalyst, one molecule of hydrogen is absorbed, and 3,8-dimethylhydrindan-1-one (XII) is formed.

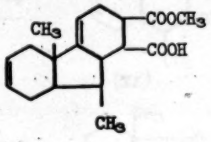
The vinyl alcohol (VI) is readily dehydrated by heating it to 130-160° with powdered potassium bisulfate, yielding about 60% of 3,8-dimethyl-1-vinyl-$\Delta^{1,5}$-tetrahydroindene (VII). The latter condenses vigorously with maleic anhydride even at room temperature (with the evolution of heat), producing an almost quantitative yield of the anhydride of 9,11-dimethyl-$\Delta^{4,6}$-octahydrofluorene-1,2-dicarboxylic acid (XIV), which yielded the 9,11-dimethyl-$\Delta^{4,6}$-octahydrofluorene-1,2-dicarboxylic acid itself upon hydrolysis and yielded the monomethyl ester of this acid, (XVI) or (XVII), when the anhydride (XIV) was heated with methanol.



(XIV)

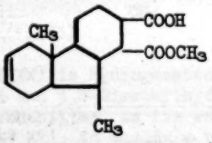


(XV)



(XVI)

(XVII)



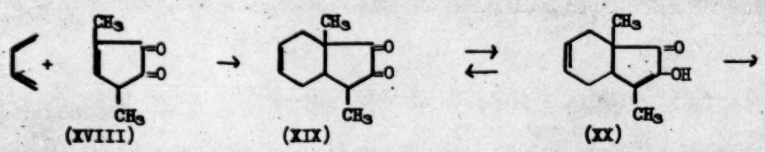
Dehydration of the vinyl alcohol (VI) by Chugaev's xanthogenate method likewise yielded the vinyltetrahydroindene (VII) described above, with a yield of some 50%, which was contaminated by sulfurous compounds, the identity of which was proved by condensation with maleic anhydride.

The vinyltetrahydroindene (VII) also condenses fairly easily with 1,3-dimethyl-Δ^1-cyclopentenone (III), resulting in a yield of some 50% of the steroid tetracyclic ketone (IX). As in other similar cases, this condensation reaction was carried out with a large excess (1000% to 1200%) of the cyclopentenone (III) for three to six hours at a temperature of 195-205°. The normal diene condensation product (VIII) that is formed in this reaction isomerizes under the reaction conditions, the double bond in the tetracyclic ketone (IX) being shifted as had been previously observed in our laboratory in other instances [2]. When the ketone (IX) is hydrogenated with a Pt catalyst, only one molecule of hydrogen is absorbed, resulting in the formation of a steroid tetracyclic ketone (X), which is transformed into the steroid tetracyclic alcohol (XI) when it is reduced by sodium in absolute propyl alcohol. Compounds (IX, X, and XI) are isomers of the respective androstane compounds (androstandienone, androstenone, and androstenol) with a methylcyclopentane ring B. According to the previously established rules of cis addition in a diene synthesis, the compounds (IX, X, and XI) ought to have a cis configuration at the points where the A – B and C – D rings are joined together.

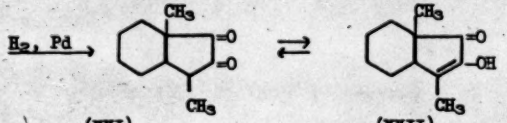
Apparently, the synthesized tetracyclic ketone (IX) is not homogeneous, since it yields a mixture of 2,4-dinitrophenylhydrazones; it may contain the

isomeric tetracyclic ketone (XXIV) with a different orientation of the cyclopentane ring D. In this connection, it is worthy of note that the steroid diketones (I and II) produced in an analogous manner are homogeneous and, hence, their diene condensations proceed in only one direction.

When the cyclopentenone (III) is oxidized by selenium dioxide in acetic acid, we get about 50% of 1,3-dimethyl-Δ^1-cyclopentene-4,5-dione (XVIII), which can be condensed even more readily with 1,3-diene compounds [3]. When the cyclopentenedione (XVIII) is heated (to 160°) with divinyl in a dioxane solution, we get a yield of about 50% of 3,8-dimethyl-Δ^5-tetrahydroindan-1,2-dione (XIX), which probably exists in the enol form (XX), which consists of colorless crystals that yield an intense color reaction with ferric chloride:



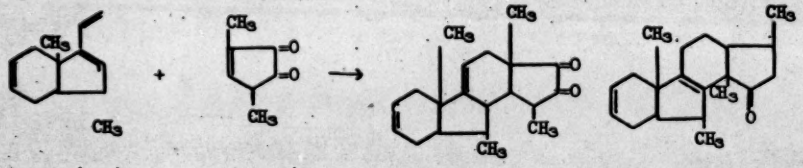
(XVIII) (XIX) (XX)



(XXI) (XXII)

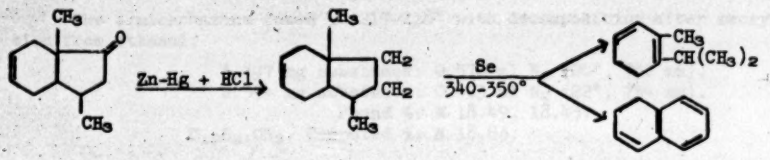
When the dione (XIX $\rightleftarrows$ XX) is hydrogenated with a Pd catalyst, one molecule of hydrogen is absorbed and 3,8-dimethylhydrindan-1,2-dione (XXI) is formed, which also exists, in all probability, as its enolic form (XXII), although, like the unsaturated dione (XIX $\rightleftarrows$ XX), it yields a bis-dinitrophenylhydrazone.

Similar keto-enol transformations were studied in detail in our laboratory in other examples [4]. The cyclopentenedione (XVIII) also condenses readily with vinylhydrindene (VII) in anhydrous benzene at 100°, yielding the crystalline tetracyclic steroid diketone (XXIII):



(VII) (XVIII) (XXIII) (XXIV)

We were interested in using the simplest examples to investigate the behavior of polycyclic compounds that contain a methylcyclopropane ring with an angular methyl group in dehydrogenation reactions and in ascertaining whether these reactions could be used to identify the polycyclic compounds referred to above. As might have been expected, 3,8-dimethyl-Δ^5-tetrahydroindan-1-one (IV) is readily reduced in a Clemmensen reduction to 3,8-dimethyl-Δ^5-tetrahydroindan (XXV), the selenium dehydrogenation of which at 340-350° is accompanied by rupture of the five-membered ring and formation of o-methylisopropylbenzene, with the partial isomerization of the five-membered ring to a six-membered ring, resulting in the formation of naphthalene:



At the present time we are using diene condensation with α,β-unsaturated cyclic ketones to effect the systematic synthesis of all sorts of steroid compounds, including their heterocyclic analogs, containing oxygen, sulfur, and nitrogen.

EXPERIMENTAL

The 1,3-dimethyl-Δ^1-cyclopentenone (III) used in our diene condensation reactions was prepared by cyclizing allyl isopropenyl ketone; it had the following constants: b.p. 163-165°; n_D^{20} 1.4660, [5].

1,3-dimethyl-Δ^1-cyclopentene-4,5-dione (XVIII) was synthesized, as described previously [4], by oxidizing 1,3-dimethyl-Δ^1-cyclopentenone (III) with selenium dioxide; it had a m.p. of 63-64°.

Condensing 1,3-dimethyl-Δ^1-cyclopentenone with divinyl. A mixture of 385 g of 1,3-dimethyl-Δ^1-cyclopentenone (III), 95 g of divinyl, and 2 g of pyrogallol was heated in a stainless-steel autoclave to 195-200° for two and a half hours in an atmosphere of nitrogen. Vacuum fractionation of the reaction mixture yielded 347 g of the original cyclopentenone and 17.5 g of 3,8-dimethyl-Δ^5-tetrahydroindan-1-one (IV), with a b.p. of 92-95° at 8 mm; n_D^{20} 1.4870. A total of 170 g of the tetrahydroindanone (IV) was synthesized in this manner. The synthesized 3,8-dimethyl-Δ^5-tetrahydroindan-1-one is a colorless, rather mobile liquid with the odor of camphor:

B.p. 90-92° at 7 mm; n_D^{20} 1.4875; d_4^{20} 0.9812; MR_D 48.11.

$C_{11}H_{16}O$. Computed: MR_D 48.14.
4.620 mg substance: 13.600 mg CO_2; 4.135 mg H_2O.
4.570 mg substance: 13.500 mg CO_2; 4.050 mg H_2O.
Found %: C 80.33, 80.61; H 10.00, 9.91.
$C_{11}H_{16}O$. Computed %: C 80.48; H 9.76.

The semicarbazone fused at 217-218° with decomposition after recrystallization from ethanol.

3.280 mg substance: 0.542 ml N_2 (20°, 745 mm).
3.970 mg substance: 0.661 ml N_2 (22°, 746 mm).
Found %: N 18.87, 18.89.
$C_{12}H_{19}ON_3$. Computed %: N 19.00.

Hydrogenating 3,8-dimethyl-Δ^5-tetrahydroindan-1-one. 3.1 g of the tetrahydroindanone (IV) was hydrogenated in 10 ml of ethanol with platinum as a catalyst. It absorbed 0.5 liter of hydrogen (1 mol). Fractionation yielded 2.6 g of 3,8-dimethylhydrindan-1-one (XII) as a colorless, rather mobile liquid with the odor of camphor:

B.p. 66-68° at 2 mm; n_D^{20} 1.4737; d_4^{20} 0.9625; MR_D 48.45.
$C_{11}H_{18}O$. Computed: MR_D 48.61.

4.01 mg substance: 11.65 mg CO_2; 3.83 mg H_2O.
Found %: 79.4; H 10.7
$C_{11}H_{18}O$. Computed %: C 79.5; H 10.8.

The semicarbazone fused at 217-218° with decomposition after recrystallization from ethanol:

3.597 mg substance: 0.578 ml N_2 (20°, 752 mm).
2.594 mg substance: 0.423 ml N_2 (22°, 754 mm).
Found %: N 18.49, 18.43.
$C_{12}H_{21}ON_3$. Computed %: N 18.83.

A test sample mixed with the semicarbazone of tetrahydroindanone (IV) fused at 211-213° with decomposition.

Condensing 3,8-dimethyl-Δ^5-tetrahydroindan-1-one with acetylene. A solution of 72 g of the ketone (IV) in 150 ml of absolute ether was saturated with acetylene for 35 minutes at a temperature of -70° (chilling with dry ice). Then a mixture of 500 ml of absolute ether with a 100% excess of tertiary potassium amylate (35 g of metallic potassium was dissolved in 200 g of tertiary amyl alcohol) was added in the course of an hour, with constant stirring and the constant passing of acetylene through the reaction mixture, to the ethereal solution at -70°. After the potassium amylate had been added, acetylene was passed through for seven hours at -70°, and the mixture was set aside to stand for 12 hours at this temperature. The next day the acetylene was passed through for another three and a half hours at room temperature. The product was treated with water (70 ml), the ether layer was separated, the aqueous layer was extracted with ether, and the ether solution was neutralized with acetic acid and desiccated with sodium sulfate. After the ether had been driven off, the product was distilled in vacuum. This yielded 56 g of 3,8-dimethyl-1-ethynyl-Δ^5-tetrahydroindan-1-ol (V) as a thick colorless liquid with a characteristic odor, which formed a copious precipitate with ammoniacal silver nitrate.

B.p. 88-90° at 4 mm; n_D^{20} 1.5100; d_4^{20} 1.0114; MR_D 56.19.
$C_{13}H_{18}O$. Computed: MR_D 56.89.

4.720 mg substance: 14.157 mg CO_2; 4.107 mg H_2O.
6.560 mg substance: 19.627 mg CO_2; 5.640 mg H_2O.
Found %: C 81.85, 81.65; H 9.73, 9.62.
$C_{13}H_{18}O$. Computed %: C 82.1; H 9.47.

Hydrogenating 3,8-dimethyl-1-ethynyl-Δ^5-tetrahydroindan-1-ol (V). 2 g of the acetylenic alcohol (V) was hydrogenated with a platinum catalyst in 10 ml of ethanol. It absorbed 749 ml of hydrogen (3 mols). Fractionation yielded 1.5 g of 3,8-dimethyl-1-ethylhydrindan-1-ol (XIII), with a b.p. of 89-91.5° at 4 mm; n_D^{20} 1.4870. Part of the synthesized 3,8-dimethyl-1-ethylhydrindan-1-ol crystallized within a day after being kept in a vacuum exsiccator above phosphoric anhydride. The large transparent crystals were separated from the liquid, washed with anhydrous ether, and analyzed.

3.710 mg substance: 10.799 mg CO_2; 4.152 mg H_2O.
Found %: C 79.44; H 12.52.
$C_{13}H_{24}O$. Computed %: C 79.59; H 12.25.

The liquid portion of the substance left after the crystals had been removed was distilled and likewise analyzed.

3.855 mg substance: 11.220 mg CO_2; 4.165 mg H_2O.
Found %: C 79.43; H 12.08.
$C_{13}H_{24}O$. Computed %: C 79.59; H 12.25.

Synthesis of 3,8-dimethyl-1-vinyl-Δ^5-tetrahydroindan-1-ol. 36.8 g of the acetylenic alcohol (V) was hydrogenated with a palladium catalyst in 50 ml of absolute ether. Hydrogenation was continued for three hours; it was stopped when

4750 ml of hydrogen (1 mol) had been absorbed. After the ether had been driven off, the product was distilled in vacuum. This yielded 33 g of 3,8-dimethyl-1-vinyl-Δ^5-tetrahydroindan-1-ol (VI), a colorless thick liquid with a slight odor:

B.p. 78-80° at 2.5 mm; n_D^{20} 1.5055; d_4^{20} 0.9855; MR_D 57.86.
$C_{13}H_{20}O$. Computed: MR_D 58.43.

4.021 mg substance: 12.009 mg CO_2; 3.830 mg H_2O.
4.774 mg substance: 14.219 mg CO_2; 4.610 mg H_2O.
Found %: C 81.50, 81.30; H 10.66, 10.80.
$C_{13}H_{20}O$. Computed %: C 81.25; H 10.42.

Dehydrating 3,8-dimethyl-1-vinyl-Δ^5-tetrahydroindan-1-ol. 8 g of the vinyl alcohol (VI) and 3.5 g of finely pulverized anhydrous potassium bisulfate were placed in a Claisen distilling flask. The mixture was heated for one hour to 130-160° in a 80-100 mm vacuum, and then all the product was driven off in a 10-mm vacuum, desiccated with calcium chloride, and redistilled. This yielded 3.5 g of 3,8-dimethyl-1-vinyl-Δ^5-tetrahydroindene (VII), a colorless, mobile liquid with a slight odor:

B.p. 73-74° at 4 mm; n_D^{20} 1.5060; d_4^{20} 0.917; MR_D 56.48.
$C_{13}H_{18}$. Computed: MR_D 56.43.
4.310 mg substance: 14.095 mg CO_2; 4.085 mg H_2O.
4.570 mg substance: 14.972 mg CO_2; 4.319 mg H_2O.
Found %: C 89.22, 89.41; H 10.60, 10.57.
$C_{13}H_{18}$. Computed %: C 89.65; H 10.35.

Condensing 3,8-dimethyl-1-vinyl-$\Delta^{1,5}$-tetrahydroindene with maleic anhydride. 1.5 g of the vinyl tetrahydroindene (VII) and 1.15 g of maleic anhydride were placed in a glass ampoule. The reaction was very rapid, with the evolution of considerable heat. It was completed by heating the mixture with 1.5 ml of anhydrous benzene for three hours in a sealed ampoule over a boiling water bath. The mass crystallized when it cooled. The crystals of 9,11-dimethyl-$\Delta^{4,6}$-octahydrofluorene-1,2-dicarboxylic acid anhydride (XIV) were recrystallized twice from petroleum ether, after which they fused at 125-126°.

4.650 mg substance: 12.814 mg CO_2; 3.145 mg H_2O.
Found %: C 75.20; H 7.57.
$C_{17}H_{20}O_3$. Computed %: C 75.00; H 7.36.

Synthesis of 9,11-dimethyl-$\Delta^{4,6}$-octahydrofluorene-1,2-dicarboxylic acid. 0.2 g of the anhydride (XIV) was boiled with 10 ml of distilled water for two hours. Recrystallization from petroleum ether yielded 9,11-dimethyl-$\Delta^{4,6}$-octahydrofluorene-1,2-dicarboxylic acid (XV) as colorless crystals that fused at 164-165° with decomposition.

2.700 mg substance: 6.941 mg CO_2; 1.906 mg H_2O.
3.060 mg substance: 7.873 mg CO_2; 2.120 mg H_2O.
Found %: C 70.16, 70.21; H 7.88, 7.75.
$C_{17}H_{22}O_4$. Computed %: C 70.34; H 7.59.

The acid was entirely insoluble in water. Titrating it in alcohol yielded the following results:

4.335 mg substance: 2.83 ml 0.01N KOH.
4.595 mg substance: 3.10 ml 0.01N KOH.
Found: M 306, 296.
$C_{17}H_{22}O_4$. Computed: M 290.

Synthesis of the monomethyl ester (XVI) or (XVII). 0.2 g of the anhydride (XIV) was boiled with 10 ml of absolute methanol for two hours. After part of the methanol had been boiled away, the colorless crystals of the monomethyl ester

(XVI) or (XVII) settled out; they fused at 127-128°.

3.414 mg substance: 8.893 mg CO_2; 2.465 mg H_2O.
4.930 mg substance: 12.889 mg CO_2; 3.640 mg H_2O.
Found %: C 71.11, 71.34; H 8.08, 8.25.
$C_{18}H_{24}O_4$. Computed %: C 71.05; H 7.89.

Titrating the monomethyl ester in alcohol yielded the following results.

5.590 mg substance: 1.88 ml 0.01 N KOH.
5.830 mg substance: 2.02 ml 0.01 N KOH.
Found: M 297, 291.
$C_{18}H_{24}O_4$. Computed: M 304.

Dehydrating 1-vinyl-3,8-dimethyl-Δ^5-tetrahydroindan-1-ol by Chugaev's xanthogenate method. 0.5 g of metallic potassium was added in small batches to a solution of 2.2 g of the vinylic tetrahydroindanol (VI) in 10 ml of absolute xylene. After no more hydrogen was evolved, the mixture was placed in a small flask fitted with a reflux condenser, closed by a tube containing calcium chloride and soda lime, and heated to 125° for two hours. 1.6 g of anhydrous hydrogen sulfide was added drop by drop to the mixture, decanted from the unreacted potassium and diluted with 10 ml of ether.* The pasty, yellowish mass was heated for an hour until the ether boiled gently, after which 2.5 g of methyl iodide was added, and heating was continued for two more hours.

After filtration of the potassium iodide precipitate, the mixture was distilled (5 mm and a bath temperature of 180-200°) after the solvent had been driven off (no cleavage occurs at a lower temperature). This yielded 1.0 g of a substance (b.p. 83-85° at 5 mm; n_D^{20} 1.5548) in the form of a yellow liquid with an unpleasant odor. After redistillation, the substance, which is vinyltetrahydroindene (VII) contaminated with sulfurous compounds, boiled at 80-82° at 5 mm; n_D^{20} 1.5537.

0.8 g of this fraction and 0.5 g of maleic anhydride were heated in 2 ml of anhydrous benzene for one hour in a sealed ampoule to 140°, after which crystals began to settle out of the hot solution. Upon cooling all the contents of the ampoule solidified. This yielded 1.0 g of crystals, which fused at 126-127.5° after being recrystallized from a mixture of benzene and petroleum ether. A test sample mixed with the 9,11-dimethyl-$\Delta^{4,6}$-octahydrofluorene-1,2-dicarboxylic acid anhydride (XIV) described above exhibited no depression. Henceforth the vinyl alcohol (VI) was always dehydrated with potassium bisulfate.

Condensing 3,8-dimethyl-1-vinyl-$\Delta^{1,5}$-tetrahydroindene with 1,3-dimethyl-Δ^1-cyclopentenone. A mixture of 5 g of the vinyltetrahydroindene (VII) and 59 g of 1,3-dimethyl-Δ^1-cyclopentenone (III) was heated for six hours to 198-200° with pyrogallol in a metallic ampoule. Fractionation of the mixture in vacuum recovered 55 g of the cyclopentenone (III) and yielded 2.6 g of the tetracyclic steroid ketone (IX), which is a thick yellow liquid with a slight odor:

B.p. 162-165° at 5 mm; n_D^{20} 1.5321; d_4^{20} 1.034; MR_D 85.11.
$C_{20}H_{28}O$. Computed: MR_D 84.84.

10.85 mg substance: 33.51 mg CO_2; 9.50 mg H_2O.
9.87 mg substance: 30.49 mg CO_2; 8.44 mg H_2O.
Found %: C 84.29, 84.30; H 9.77, 9.57.
$C_{20}H_{28}O$. Computed %: C 84.50; H 9.89.

Prior to analysis the product was kept in a vacuum exsiccator for two days over phosphoric anhydride.

The 2,4-dinitrophenylhydrazone of the synthesized steroid ketone (IX) precipitated successively – first the high-melting part, and then – from the mother

*This was accompanied by theevolution of considerable heat.

liquor – the low-melting part. After recrystallization from methanol, the low-melting part fused at 124-125° with decomposition.

4.478 mg substance: 0.580 ml N_2 (23°, 753 mm).
4.545 mg substance: 0.665 ml N_2 (23°, 752 mm).
Found %: N 14.80, 16.69.
$C_{26}H_{32}O_4N_4$. Computed %: N 12.07.

After recrystallization, the high-melting part of the product fused at 224-225° with decomposition.

3.450 mg substance: 0.450 ml N_2 (23°, 750 mm).
Found %: N 14.84.
$C_{26}H_{32}O_4N_4$. Computed %: N 12.07.

There remained still another part of the substance, which had not dissolved in the methanol and fused at a temperature above 300° with decomposition.

3.230 mg substance: 0.417 ml N_2 (24°, 733 mm).
3.370 mg substance: 0.455 ml N_2 (23°, 733 mm).
Found %: N 14.31, 15.01.
$C_{26}H_{32}O_4N_4$. Computed %: N 12.07.

Thus, analysis of all the three samples of the dinitrophenylhydrazones gave poorly reproducible results, with a much higher percentage of nitrogen than was called for by theory.

This anomaly in the dinitrophenylhydrazones of the polycyclic ketones has been observed in our laboratory in a number of other instances as well [9], and the cause of this phenomenon is as yet unknown. Perhaps some of the polycyclic ketones of the steroid type and their dinitrophenylhydrazones form stable molecular compounds with dinitrophenylhydrazine, which would explain the observed discrepancies in their analysis.

Hydrogenating the tetracyclic steroid ketone (IX). 2.2 g of the steroid ketone (IX) was hydrogenated with a platinum catalyst in 10 ml of absolute dioxane. 176 ml of hydrogen (1 mol) was absorbed. Fractionation yielded 1.5 g of a tetracyclic steroid ketone (X) as a viscous liquid:

B.p. 158° at 4 mm; n_D^{20} 1.5225; d_4^{20} 1.033; MR_D 84.51.
$C_{20}H_{30}O$. Computed: MR_D 85.30.

9.95 mg substance: 30.44 mg CO_2; 9.10 mg H_2O.
16.48 mg substance: 50.39 mg CO_2; 15.12 mg H_2O.
Found %: C 83.74, 83.53; H 10.23, 10.26.
$C_{20}H_{30}O$. Computed %: C 83.91; H 10.4.

Prior to analysis the product was kept above phosphoric anhydride in a vacuum exsiccator for three days.

The 2,4-dinitrophenylhydrazone of the steroid ketone (X) fused at 200-202° (with decomposition) after it had been recrystallized from methanol.

2.200 mg substance: 0.259 ml N_2 (23°, 750 mm).
Found %: N 13.40.
$C_{26}H_{34}O_4N_4$. Computed %: N 12.00.

Reducing the tetracyclic steroid ketone (X). 1.9 g of the tetracyclic steroid ketone (X) was reduced in 55 ml of absolute propyl alcohol with 5 g of metallic sodium. The usual treatment and vacuum distillation of the product yielded 1.5 g of a tetracyclic steroid alcohol (XI) as a viscous liquid with a b.p. of 167-170° at 5 mm.

11.17 mg substance: 34.04 mg CO_2; 11.05 mg H_2O.
12.38 mg substance: 37.88 mg CO_2; 12.54 mg H_2O.
Found %: C 83.17, 83.50; H 11.07, 11.35.
$C_{20}H_{32}O$. Computed %: C 88.33; H 11.11.
0.2540 mg substance: 19.6 ml CH_4 (22°, 743 mm).
0.1910 mg substance: 12.5 ml CH_4 (19°, 730 mm).
Found %: OH 5.63, 5.53.
$C_{20}H_{31}OH$. Computed %: OH 5.9.

Condensing 1,3-dimethyl-Δ^1-cyclopentene-4,5-dione with divinyl. 5 g of the dione (XVIII) and 20 g of divinyl were dissolved in absolute dioxane and heated for six hours in a metallic ampoule to 158-162°. The mass that remained after the dioxane had been driven off crystallized. Recrystallization from ethyl alcohol yielded 2.3 g of the colorless crystals of 3,8-dimethyl-Δ^5-tetrahydroindane-1,2-dione (XIX $\rightleftarrows$ XX) with a m.p. of 125-126°.

4.450 mg substance: 12.083 mg CO_2; 3.170 mg H_2O.
4.997 mg substance: 13.587 mg CO_2; 3.510 mg H_2O.
Found %: C 74.10, 74.20; H 7.97, 7.85.
$C_{11}H_{14}O_2$. Computed %: C 74.10; H 7.86.

The substance colored a solution of ferric chloride bright violet. Its dinitrophenylhydrazone fused at 225-226° with decomposition after it had been recrystallized from ethyl alcohol.

2.979 mg substance: 0.512 ml N_2 (25°, 746 mm).
3.600 mg substance: 0.612 ml N_2 (26°, 746 mm).
Found %: N 19.33, 19.33.
$C_{23}H_{22}O_8N_8$. Computed %: N 20.82.
$C_{17}H_{18}O_5N_4$. Computed %: 16.59.

Hydrogenating 3,8-dimethyl-Δ^5-tetrahydroindane-1,2-dione. 1 g of the dione (XIX $\rightleftarrows$ XX) was hydrogenated with a platinum catalyst in 50 ml of absolute ether. 110 ml of hydrogen (1 mol) was absorbed. Recrystallization from petroleum ether yielded 0.9 g of the colorless crystals of 3,8-dimethylhydrindane-1,2-dione (XXI $\rightleftarrows$ XXII) with a m.p. of 104-104.5°.

10.27 mg substance: 27.51 mg CO_2; 8.35 mg H_2O.
12.32 mg substance: 33.04 mg CO_2; 9.88 mg H_2O.
Found %: C 73.10, 73.18; H 9.10, 8.99.
$C_{11}H_{16}O_2$. Computed %: C 73.30; H 8.88.

The 2,4-dinitrophenylhydrazone fused at about 200° with decomposition after it had been recrystallized from ethyl alcohol.

3.580 mg substance: 0.653 ml N_2 (24°, 747 mm).
3.813 mg substance: 0.685 ml N_2 (25°, 746 mm).
Found %: N 20.60, 20.20.
$C_{23}H_{24}O_8N_8$. Computed %: N 20.74.

Condensing 3,8-dimethyl-1-vinyl-$\Delta^{1,5}$-tetrahydroindene with 1,3-dimethyl-Δ^1-cyclopentene-4,5-dione. 1.5 g of the vinyltetrahydroindene (VII) and 1 g of the cyclopentenedione (XVIII) were dissolved in 2.5 g of absolute benzene and heated for six hours in a metallic ampoule over a boiling water bath. After the benzene had been driven off, what was left was a sticky mass, which was dissolved in ethanol. The solution yielded 0.7 g of the crystals of a tetracyclic diketone (XXIII), which fused at 165-167° after it had been recrystallized from ethanol.

4.420 mg substance: 13.069 mg CO_2; 3.560 mg H_2O.
4.500 mg substance: 13.328 mg CO_2; 3.675 mg H_2O.
Found %: C 80.70, 80.84; H 8.94, 9.13.
$C_{20}H_{26}O_2$. Computed %: C 80.53; H 8.73.

Reducing 3,8-dimethyl-Δ^5-tetrahydroindan-1-one by the Clemmensen method. A solution of 5 g of dimethyltetrahydroindanone (IV) in 25 ml of ethyl alcohol was added in small batches, in the course of two hours, to a boiling mixture of 5 ml of water, 5 ml of ethyl alcohol, 15 ml of concentrated hydrochloric acid, and zinc amalgam, prepared from 15 g of granulated zinc and 1.5 g of mercuric chloride. Then the mixture was heated to boiling for 8 hours. During this time 10 ml of concentrated hydrochloric acid was added in separate batches. The mixture was diluted with 15 ml of water and extracted with ether; the ether extract was desiccated with magnesium sulfate, and the ether was driven off. Distillation yielded 4.3 g of 3,8-dimethyl-Δ^5-tetrahydroindane (XXV) with a b.p. of 44-47° at 8.5 mm; n_D^{20} 1.4674.

Dehydrogenating 3,8-dimethyl-Δ^5-tetrahydroindane with selenium. 4.3 g of the tetrahydroindane (XXV) and 5 g of powdered selenium were heated to 340-350° for five hours in a sealed ampoule. When the ampoule was opened, hydrogen selenide was liberated copiously. The mixture was extracted with benzene, and the benzene solution was washed with 60% sulfuric acid, water, and 10% caustic soda, and desiccated with magnesium sulfate. Fractionation over metallic sodium yielded:

Fraction 1: b.p. 95-98° at 35 mm; n_D^{20} 1.5002, 2.2 g.

Fraction 2: b.p. 73-76° at 6 mm; 0.4 g.

The first fraction, which was o-methylisopropylbenzene [7], boiled at 176-177° at atmospheric pressure after being redistilled.

n_D^{20} 1.5002; d_4^{20} 0.8744: MR_D 45.14. Computed: 44.78.

5.873 mg substance: 19.03 mg CO_2; 5.53 mg H_2O.
13.78 mg substance: 45.08 mg CO_2; 13.10 mg H_2O.
Found %: C 89.3, 89.3; H 10.6, 10.6.
$C_{10}H_{14}$. Computed %: C 89.5; H 10.5.

The second fraction solidified in the condenser and fused at 79.5° after recrystallization from alcohol. A test sample mixed with standard naphthalene exhibited no depression.

SUMMARY

The complete synthesis of steroid compounds (IX, X, XI, AND XXIII), belonging to the B-norandrostane series with a methylcyclopentane ring B, has been effected by means of diene condensations.

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*See CB translation p. 581 ff. and 697 ff.

**See CB translation p. a 211 ff.

THE CONDENSATION OF TETRAMETHYLBUTYNEDIOL WITH PHENOL

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A paper by one of the present authors and S.G.Kuznetsov [1] has dealt with the condensation of tetraphenylbutynediol with phenol and with cresol [2]. The objective of our research has been a study of the reaction of phenol with an acetylenic glycol containing aliphatic radicals, namely: tetramethylbutynediol, using the same catalyst, sulfanilic acid.

It has been found that tetramethylbutynediol can also condense with phenol, though the reaction takes place under more severe conditions. Tetraphenylbutynediol, for instance, adds a molecule of phenol when it is boiled with sulfanilic acid in a benzene solution. Tetramethylbutynediol does not react under these conditions, even when it is heated for 8 hours. The reaction took place only when heating was continued for 6-8 hours to 138-140° in a xylene solution, but this involved considerable tarring. Increasing the quantity of sulfanilic acid affects neither the reaction rate nor the product yield, while increasing the proportion of the phenol from 0.2 mol to 0.4 mol per 0.1 mol of the glycol increases the yield of the products of the glycol-phenol condensation.

In a desire to speed up the reaction, we made several tests with a more active catalyst, viz.: activated Chasovyarsk clay. It was found, however, that here, too, heating to 138-140° is required, inasmuch as the reaction did not take place in boiling toluene. As a result, the yield of condensation products dropped, while the quantity of tar rose to 60-65%.

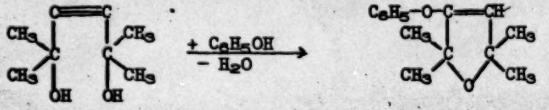
The experiments were made with the same apparatus that was used in our previous research, i.e., a flask with a reflux condenser and a trap to catch the water evolved during the reaction. While the mixture was heated, about 2 mols of water were evolved per 0.1 mol of the glycol. This might have pointed to the formation of a diphenyl ether of the glycol, but analysis of the reaction products indicated that the phenol is added at the triple bond and does not react with the glycol's hydroxyl groups. The evolution of one molecule of water is due to the formation of a furan ring, while the formation of the rest of the water is apparently due to the dehydration of the glycol, which gives rise to a hydrocarbon – dimethyldivinylacetylene – which is readily polymerized. This may also explain the copious formation of tar. To be sure, no water is evolved when tetramethylbutynediol is heated with sulfanilic acid in a xylene solution when no phenol is present, perhaps because the temperature of this boiling mixture is not high enough. But heating the xylene solution of tetramethylbutynediol with activated clay actually results in dehydration, and in this experiment we were able to recover, in addition to the tar, some alcohol of the vinyl-acetylene series, produced from the

*Deceased.

glycol by the splitting cut of one molecule of water.

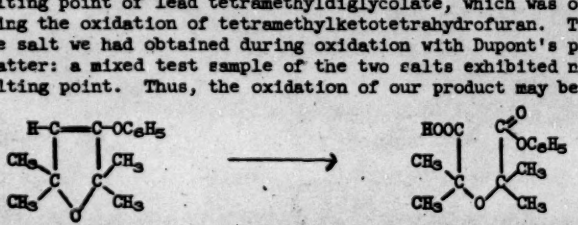
We judged that the reaction had come to an end when no more water was evolved. The xylene solution was then decanted from the sulfanilic acid, which is insoluble in xylene, and distilled with steam, after which it was fractionated. The mixture can be fractionated at ordinary pressure, but this causes part of the end products to tar. A residue of dark tar was left in the distilling flask, from which we were unable to recover any definite product, except for a minute quantity of the unreacted glycol. An oily layer floated above the water in the receiver; it was distilled at reduced pressure after it had been separated from the water. After the xylene and the excess phenol had been driven off, we got two fractions, which distilled at 108-111° and 128-131° at 8 mm. Judging from their analyses and molecular weight, both of these substances had the formula $C_{14}H_{18}O_2$.

The yield of the substance with a b.p. of 128-131° at 8 mm was 15-20% of the theoretical. It is a light-yellowish liquid with a pungent, characteristic odor, which is readily soluble in organic solvents. It is insoluble in alkalies, it decolorizes bromine water, and it exhibits no reaction for a hydroxyl group. These properties led us to assume that the substance in question is 2,2,-5,5-tetramethyl-3-phenoxy-2,5-dihydrofuran, which is formed by the addition of one molecule of phenol to the triple bond, followed by the detaching of one molecule of water and the constitution of a furan ring:



This formula was confirmed by the following experiments. When the unknown substance was heated with hydriodic acid, a molecule of phenol split away, as was proved by its conversion into tribromophenol. This corroborated the presence of a phenoxy group.

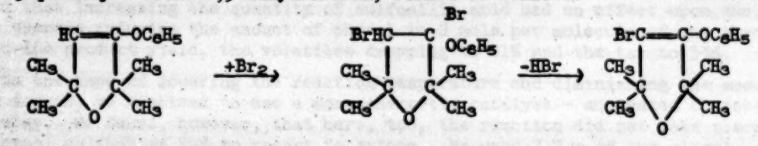
Oxidation with potassium permanganate yielded acetic and formic acids, as well as an oily liquid with a b.p. of 120-125° at 8 mm. A large quantity of the same liquid was obtained when we oxidized our product with chromic anhydride. It did not form a semicarbazone. When it was heated with 10% caustic potash, it saponified, yielding phenol. After the solution of potassium salts had been evaporated to dryness, the salt of the organic acid was extracted with alcohol, the mineral salts were filtered out, the alcoholic solution was evaporated, and the residue was dissolved in water. Precipitation with a saturated solution of lead acetate yielded a crystalline precipitate of a lead salt with a m.p. of 266°; this is the melting point of lead tetramethyldiglycolate, which was obtained by Dupont [3] during the oxidation of tetramethylketotetrahydrofuran. To prove the identity of the salt we had obtained during oxidation with Dupont's product, we prepared the latter: a mixed test sample of the two salts exhibited no depression of the melting point. Thus, the oxidation of our product may be represented as follows:



To demonstrate the presence of a double bond, the product was thoroughly hydrogenated with platinum. It was found that it readily adds two atoms of hydrogen to the molecule, after which the reaction comes to an end. The hydrogenation product, 2,2,5,5-tetramethyl-3-phenoxytetrahydrofuran, is a colorless oily liquid

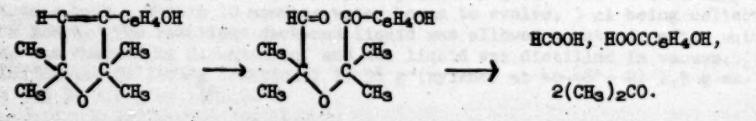
with a b.p. of 132-134° at 8 mm.

When a chloroform solution of 2,2,5,5-tetramethyl-3-phenoxy-2,5-dihydrofuran is reacted with bromine at 0°, two atoms of bromine are added fairly easily, without tarring, but the resultant dibromide gives off one molecule of hydrogen bromide at room temperature, tarring noticeably as it does so. We succeeded in recovering a small quantity of crystals with a m.p. of 137°, whose composition was that of a monobromide. It must be assumed that the monobromide is 2,2,5,5-tetramethyl-3-phenoxy-4-bromo-2,5-dihydrofuran, formed as follows:



The instability of such dibromides has been commented on previously [4].

The other condensation product of tetramethylbutynediol with phenol, with a b.p. of 108-110° at 8 mm, is a colorless oily liquid with a characteristic acrid odor. It turns somewhat darker when stored for 5-6 months, is readily soluble in organic solvents, and decolorizes bromine water. Its Chugaev-Tserevitinov reaction indicates the presence of one hydroxyl group. These results seem to indicate that its structure is that of 2,2,5,5-tetramethyl-3-hydroxyphenyl-2,5-dihydrofuran. Oxidation with potassium permanganate or with chromic anhydride yielded acetone and formic and p-hydroxybenzoic acids, which bears out the formula 2,2,5,5-tetramethyl-3-p-hydroxyphenyl-2,5-dihydrofuran:



The results of platinum hydrogenation also served to confirm this formula. Two hydrogen atoms were added to the molecule, yielding a liquid with a b.p. of 112-113° at 8 mm: 2,2,5,5-tetramethyl-3-p-hydroxyphenyltetrahydrofuran.

The action of bromine upon the condensation product yielded a crystalline dibromide with a total yield of 17%, the reaction being accompanied by considerable tarring. Inasmuch as no hydrogen bromide was evolved during the reaction, we must attribute the structure of 2,2,5,5-tetramethyl-3-p-hydroxyphenyl-3,4-dibromotetrahydrofuran to the synthesized dibromide.

EXPERIMENTAL

Condensation of tetramethylbutynediol with phenol. 7.1 g of tetramethylbutynediol (0.05 mol), 18.4 g of phenol (0.2 mol), 0.5 g of sulfanilic acid, and 60 ml of benzene were heated to boiling for 8 hours in a flask connected to a trap for water and to a reflux condenser. No water was evolved; nothing was recovered, with the exception of some tar and the initial products. The same results were obtained when the benzene was replaced by toluene and the reaction temperature was raised to 110-112°; though some water was evolved, only a few drops of a yellowish liquid were recovered. Further experiments were, therefore, conducted in a xylene solution at 138-142° (thermometer in the liquid).

14.2 g (0.1 mol) of the glycol, 37.6 g (0.4 mol) of phenol, and 60 ml of xylene were heated to boiling for 3 hours; no water was evolved, nor were other

signs of a reaction noticed. Then 1 g of sulfanilic acid was added to the somewhat chilled mixture. 15-20 minutes after the mixture began to boil, drops of water began to fall to the bottom of the trap. The evolution of water was most intensive during the second and third hours of boiling. No more water was evolved after the boiling had gone on for 5 hours. A total of 3.5 ml (nearly 0.2 mol) of water was evolved. We obtained 31% of volatile products and 42% of tar, based on the glycol.

Subsequent experiments with various compositions of the reaction mixture indicated that increasing the quantity of sulfanilic acid had no effect upon the yield, whereas reducing the amount of phenol to 2 mols per molecule of the glycol lowered the product yield, the volatiles dropping to 21% and the tar to 33%.

In the hope of lowering the reaction temperature and diminishing the amount of tar formed, we resolved to use a more energetic catalyst – activated Chasovyarsk clay. We found, however, that here, too, the reaction did not take place in toluene, so that we had to resort to xylene. We used 7.2 g of the glycol, 18.7 g of phenol, 0.75 g of the clay, and 60 ml of xylene. The reaction set in as soon as boiling started; it ended 3 hours later. 1.8 ml of water was evolved. A total of some 8% of condensation products was obtained. The remainder consisted of tar (60%) and some 30% of various substances, one of which boiled at 150-160°, while the other boiled at 116-131° (both at 8 mm). In contrast to the products of the phenol condensation, the latter decomposed when distilled at ordinary pressure. The results of this experiment forced us to conclude that the principal reaction taking place here was the dehydration of the glycol. To check this we made a test under the same conditions, but without any phenol added.

14.2 g of the glycol, 120 ml of xylene, and 1.5 g of the activated clay were brought to a boil. Within 10 minutes water began to evolve, 3 ml being collected within 2 hours. The resultant dark-red liquid was allowed to stand, after which the clay was removed by decantation, and the liquid was distilled in vacuum. This yielded the following fractions: 1) 96 g (xylene) at 40-48°; 2) 1.5 g at 66-70°; and 3) 3.2 g at 118-120°.

Fraction 2 distils at 158-160° at standard pressure, and liberates large quantities of gas when reacted with ethylmagnesium bromide; it apparently represents the product of the incomplete dehydration of tetramethylbutynediol, $CH_2{=}C(CH_3){-}C{\equiv}C{-}C(OH)(CH_3)_2$, obtained by Dupont. The third fraction does not react with ethylmagnesium bromide and decomposes when heated above 160°. Analysis indicated that this is an unsaturated hydrocarbon.

0.0670 g substance: 0.2229 g CO_2; 0.0573 g H_2O.
Found %: C 90.87; H 9.57.
C_8H_{10}. Computed %: C 90.56; H 9.43.

Hence, heating tetramethylbutynediol with activated clay actually results in dehydration of the glycol, less of its condensation products with phenol being recovered than when sulfanilic acid is employed.

After the xylene had been eliminated, fractionation (at 8 mm) yielded two fractions, with a b.p. of 108-111° and 128-131°. Analysis showed that the first fraction is 2,2,5,5-tetramethyl-3-p-phenoxy-3-p-hydroxyphenyl-2,5-dihydrofuran, and the second was 2,2,5,5-tetramethyl-3-phenoxy-2,5-dihydrofuran.

2,2,5,5-Tetramethyl-3-phenoxy-2,5-dihydrofuran. This substance is a slightly yellowish, oily liquid:

B.p. 130° (at 8 mm); d_{15}^{15} 0.9947; n_D^{12} 1.52375; MR_D 65.24.
$C_{14}H_{18}O_2$. Computed: MR_D 63.87.

The substance is insoluble in water, but readily dissolves in organic solvents,

decolorizes bromine water, does not react with ethylmagnesium bromide, and is insoluble in caustic soda.

0.2010 mg substance: 0.5652 g CO_2; 0.1482 g H_2O.
0.0658 g substance: 18.999 g benzene: Δt 0.11°.
Found %: C 76.72; H 8.28; M 213.4.
$C_{14}H_{18}O_2$. Computed %: C 77.06; H 8.26; M 218.

To demonstrate the presence of a phenoxy group, we boiled 0.3 g of the substance for 3 hours with 10 ml of hydriodic acid (sp. gr. 4.7) and 3 ml of acetic acid. The mixture was distilled with steam, and the distillate was treated with sodium sulfite to eliminate the iodine and then with bromine water. This yielded a precipitate which fused at 95° after crystallization and exhibited no depression of the melting point in a mixed test sample with tribromophenol.

1.09 g of the substance (0.05 mol) absorbed 126 ml of hydrogen (18.5°, 750 mm) in 40 minutes when hydrogenated in an alcoholic solution with 0.351 g of platinum black, which represents two molecules of hydrogen added per molecule of the substance. The resultant product, a colorless, oily liquid, had the following constants:

B.p. 132-134° (at 8 mm); d_{12}^{12} 0.9962; n_D^{12} 1.51354; MR_D 64.38.

Computed: MR_D 64.34.

Oxidation of tetramethylphenoxydihydrofuran by potassium permanganate in aqueous solution, followed by the usual treatment, yielded 0.7 g of neutral products as a liquid that had the odor of the original substance, plus formic and acetic acids. The former product was demonstrated by its blackening a silver salt when heated and its being reduced by a solution of corrosive sublimate. Crystals of the silver salt settled out after the reduced silver had been filtered out and the solution had cooled.

0.1282 g substance: 0.0824 g Ag.
Found %: Ag 64.27.
$C_2H_3O_2Ag$. Computed %: Ag 64.66.

Inasmuch as these results did not give any definite proof of the structure of the substance, we oxidized it with chromic anhydride. 2.45 g of chromic anhydride was added in small batches in the course of 3 hours to a solution of 2 g of the substance in 20 ml of acetic acid, after which the mixture was heated over a water bath for 15 minutes. The reaction mixture was diluted with water, and the oxidation products were extracted three times with petroleum ether. The extract was washed with water, the ether was driven off, and the residue was distilled at 8 mm. This yielded 0.9 g of a liquid with a b.p. of 120-125°. It forms no semicarbazone. A small quantity of the same liquid was also obtained by oxidizing with potassium permanganate. Saponification took place when the substance was heated with 10% potassium hydroxide; phenol was recovered when carbon dioxide was passed through the chilled solution.

After extraction with ether, it distilled at 180° and solidified into crystals. The solution of the residual potassium salts was evaporated to dryness, and the salts of organic acids were extracted with alcohol while boiling. The spirit was driven off, and the residue was dissolved in water and precipitated by a solution of lead acetate. Upon chilling, a finely crystalline precipitate of a lead salt with a m.p. of 266° settled out; this is the temperature given by Dupont [3] for lead tetramethyldiglycolate, $HOOC-C(CH_3)_2-O-C(CH_3)_2-COOH$.

To prove the identity of the salt we had synthesized and the salt of tetramethyldiglycolic acid, we prepared the latter according to Dupont's instructions. This was done by heating a mixture of 6 g of tetramethylbutynediol, 1.2 g of mercuric sulfate, and 30 ml of water to 80° for 20 minutes; the resulting tetra-

methyltetrahydroketofuran was driven off with steam, distilled at 149-150° after the water had been separated out, and oxidized by potassium permanganate. After the manganese dioxide had been removed, the neutral solution was precipitated with lead acetate, and the deposit of the lead salt was filtered out and recrystallized from hot water.

The crystals fused at 266° and exhibited no depression when mixed in a test sample with the substance we had produced by oxidizing tetramethylphenoxydihydrofuran.

We made an effort to add bromine to the tetramethylphenoxydihydrofuran. 2 g of the substance was dissolved in 50 ml of chloroform, and a solution of 1.44 g of bromine in 14 ml of chloroform was added drop by drop to the former solution, with stirring and chilling with ice. Bromination was rapid, without tarring, and without the evolution of any hydrogen bromide. The amount of bromine required for the addition of two bromine atoms to the double bond was consumed in 30 minutes. When we tried to add more bromine, hydrogen bromide was evolved. The bromide was observed to decompose violently when the reaction product was poured into a distilling flask and when the chloroform was driven off in vacuum, with the evolution of hydrogen bromide and the occurrence of considerable tarring. The next day crystals were observed in the beaker containing the bromide. They were placed on an unfired porcelain plate and recrystallized from ether the next day. M.p. 137-138°. Analysis indicated that this was a monobromide.

0.1123 g substance: 0.0725 g AgBr (Carius).
Found %: Br 27.47.
$C_{14}H_{17}O_2Br$. Computed %: Br 26.94.

2,2,5,5-Tetramethyl-3-p-hydroxyphenyl-2,5-dihydrofuran. This is a colorless, oily liquid with an acrid, characteristic odor:

b.p. 108-110° (at 8 mm); d_{12}^{12} 0.9966; n_D^{12} 1.52218; MR_D 64.25.
$C_{14}H_{18}O_2$. Computed: MR_D 63.75.

0.0580 g substance: 0.1640 g CO_2; 0.0410 g H_2O.
0.1231 g substance: 15.70 g benzene: Δt 0.19°.
Found %: C 77.11, H 7.91; M 210.5.
$C_{14}H_{18}O_2$. Computed %: C 77.06; H 8.25; M 218.

0.0714 g substance: 6.9 ml ethane (0°, 760 mm).
$C_{14}H_{17}O(OH)$. Computed ethane: 7.3 ml.

When 1.1 g of the substance was hydrogenated for 25 minutes in 50 ml of ether with 0.35 g of platinum black, 125 ml of hydrogen was added, after which the reaction came to a stop. This quantity is equivalent to 2 hydrogen atoms per molecule of the substance (theoretically, 119.2 ml are required). The hydrogenation product, 2,2,5,5-tetramethyl-3-p-hydroxylphenyltetrahydrofuran, is a liquid with a b.p. of 112-113° at 8 mm; d_{12}^{12} 0.9981; n_D^{12} 1.51734; MR_D 64.37; Computed MR_D 64.21.

2 g of tetramethylhydroxyphenyldihydrofuran was dissolved in 20 ml of glacial acetic acid and oxidized with 3 g of chromic anhydride, which was added in the course of 3 hours in small batches, with constant stirring. Then the reaction mixture was heated for 15 minutes over a water bath, diluted with water, and extracted with ether. The ether extract was washed with water and a soda solution and desiccated with sodium sulfate. After the ether and the acetone had been driven off, some of the initial substance and a reddish tar were recovered. The aqueous solution and the wash water were distilled with steam. Formic acid was found in the distillate (blackening a silver salt and reduction by corrosive sublimate). The concentrated solution of the difficultly volatile acids was extracted with ether for 24 hours in an extractor. Driving off the ether yielded p-hydroxybenzoic acid, which fused at 213° after crystallization from water and

yielded phenol when heated with soda lime. A slightly warmed ammoniacal solution was precipitated with silver nitrate, acicular crystals of the silver salt setling out when the solution was cooled.

0.1370 g substance: 0.0597 g Ag.
Found %: Ag 43.58.
$C_7H_5O_3Ag$. Computed %: Ag 43.90.

2 g of tetramethyl-p-hydroxyphenyldihydrofuran was dissolved in 50 ml of chloroform and 1.44 g of bromine dissolved in 14 ml of chloroform was added to the solution at -5°. The reaction soon slowed down to the point where it could be carried out at room temperature. But here, too, the bromine was added so slowly that the amount of bromine remaining after 5 hours was added in one batch, and the mixture was set to stand overnight. Driving off the chloroform left behind a dark liquid with an acrid odor. Crystals separated out after the mixture had stood in the exsiccator for 5 days. They fused at 131-132°.

0.0950 g substance: 0.0958 g AgBr (Carius).
Found %: Br 42.83.
$C_{14}H_{18}Br_2$. Computed %: 42.30.

Hence, these crystals apparently are a dibromide – 2,2,5,5-tetramethyl-3-p-hydroxyphenyl-3,4-dibromotetrahydrofuran.

SUMMARY

It has been shown that in the presence of sulfanilic acid tetramethylbutynediol condenses with phenol, two products being formed: 2,2,5,5-tetramethyl-3-phenoxy-2,5-dihydrofuran and 2,2,5,5-tetramethyl-3-p-hydroxyphenyl-2,5-dihydrofuran. The products of the hydrogenation and the bromination of these substances have also been synthesized. It is harder to add phenol at the triple bond than in the case of tetraphenylbutynediol, and the reaction is accompanied by dehydration of the acetylenic glycol.

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NEW TYPES OF TERPENE TRANSFORMATIONS

II. THE ACTION OF CHLORINE UPON α- AND β-PINENES

D. Tishchenko and B. Matveev

In our report [1] it was asserted, on the basis of the similarity between the simplest quaternary olefins and the terpenes, that we might be able to constitute practically unknown and inaccessible allyl monochlorides of the terpenes by reacting the latter with chlorine. It was shown that the references in the literature do not confirm this possibility, but neither do they deny it, and that they are entirely inadequate for the outlining of any sort of general scheme for this reaction. The reasons for the failure in all previously known research in this field were disclosed (they are rooted in procedural errors, both in the approach to the problem and in its solution), and the experimental conditions were specified that would ensure the successful solution of the problem.

The present research is the first of a series of completed studies devoted to the action of chlorine upon the terpenes. Its results fully confirm the views set forth by us in Report I; moreover, they finally shed light upon the evaluation of the various schemes showing the action of chlorine upon olefins with a branched double bond. Four such schemes have been proposed:

1) The scheme put forward by M.D.Lvov: the addition of chlorine at the double bond; the partial irregular decomposition of the dichloride into an allyl monochloride, with the double bond shifted and hydrogen chloride liberated [2];

2) The scheme advanced by one of the authors of the present paper: the addition of the positive part of the polarized chlorine molecule to the end of the olefin's double bond that is negatively polarized by the inductive actions of the substituents and the capture of the chlorine anion by the most highly "protonized" β-carbon atom, with hydrogen chloride evolved and the double bond shifted (Lvov's "anomalous" reaction), or the addition of the chlorine anion to the positively polarized end of the double bond, with a dichloride formed (the "classic" reaction, a side reaction that is retarded by steric hindrances) [3];

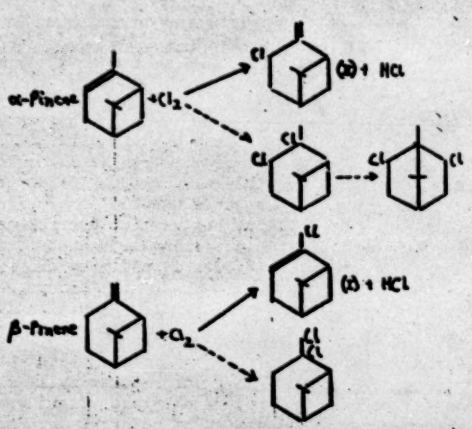
3) The "substituent" scheme of American chemists: two independent reactions taking place simultaneously: a) the addition of chlorine to the double bond; and b) chlorine replacing the hydrogen atoms (the double bond playing no part in the reaction) [4]; and

4) The same sort of "substituent" scheme of a dualistic mechanism, with the restriction that only the hydrogen atoms attached to the double bond in the α-position can be replaced [5].

The scheme proposed by M.D.Lvov, which comes closer to the actual facts than the notions put forward by the American authors and was quite progressive at the

time of its publication, has already been disproved by us [6]. Some American chemists have rejected the scheme of "substituent" chlorination [7] in favor of our scheme, while others have not. Hass, the author of the scheme of "substituent" α-chlorination, is among those who have not abandoned it. In spite of the fact that both of these schemes have been disproved convincingly enough by our previous papers [3], these "substituent" notions still are current today, even in our own chemical journals [8]. The data we have obtained in our present research should again and, we hope, once and for all, dispose of these schemes.

According to our notions, the action of chlorine upon α- and β-pinenes may be represented as follows:



According to the the "substituent" scheme we should expect to get seven monochlorides with shifted double bonds for both the α- and β-pinenes [9].

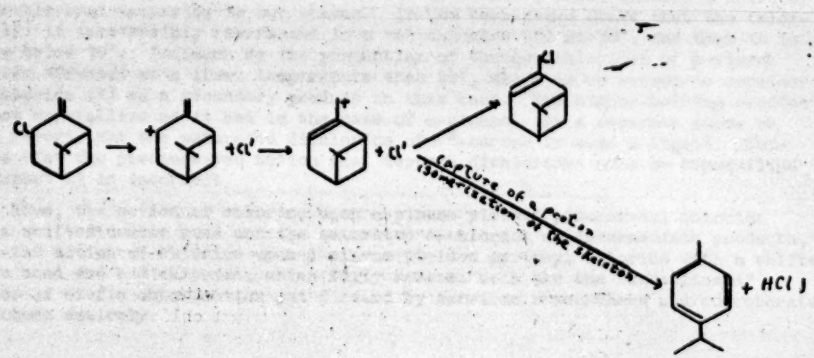
According to the "α-substituent" scheme, the α-pinene should give rise to three monochlorides with an unshifted double bond, while the β-pinene sould form two such monochlorides. It should be noted that the author of the "α-substituent" scheme does not explain the reasons for the ability of the α-hydrogen atoms to enter into substitution reactions.

We reacted α- and β-pinenes with chlorine under the following conditions: no more than 0.5 mol of chlorine was reacted with 1 mol of the terpene; the temperature of the reaction mixture was kept below -3° by means of external chilling and regulating the chlorine supply; an excess of sodium bicarbonate, which does not react with anhydrous chlorine, was placed in the reaction vessel to absorb the liberated hydrogen chloride; and local increases in the concentration of the chlorine or the hydrogen chloride were prevented by vigorous stirring of the reaction mixture (all the $NaHCO_3$ went into suspension). These measures enabled us to prevent any reaction of the original terpenes or of its transformation products with the hydrogen chloride and largely to diminish the reaction of the chlorine with the accumulated monochlorides of the terpenes (cf below), which enabled us to get a basic picture of the reaction.

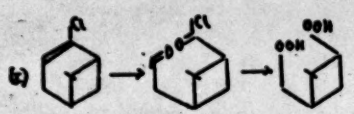
Our first experiments on the reaction of chlorine with α-pinene yielded results not in agreement with our diagram: we got myrtenyl chloride (I) and dichloride instead of of pinocarveol chloride (II)and dichloride. Inasmuch as we separated

the reaction products by fractionating them in a tower at a pressure of 13 mm, and the monochloride fraction distilled at 87-88°, the whole reaction product had to be heated to at least 115-120° to ensure adequate temperature transfer to overcome the dynamic resistance of the tower packing and to separate the monochloride from the higher-boiling polychlorides. We had previously proved that the temperature threshold for isomerization of chlorides of the allyl type is no higher than 70° [10]. In the present case, the isomerization of (II) to (I) must be rapid and irreversible, since 5-7 calories of energy are liberated when the semicyclic double bond is shifted to the ring (cf Report 1). When the product is distilled under the specified conditions, hydrogen chloride begins to evolve vigorously after the α-pinene has been separated out and the temperature within the distilling flask has reached approximately 110°, up to 26% p-cymene being distilled together with it, based on the amount of chlorine introduced into the reaction. Then the liberation of the HCl ceases, and the monochloride distils over. Toward the end of this distilation the contents of the flask suddenly solidify into a crystalline paste. Drawing off the liquid makes it possible to secure a dichloride with a yield of 17%, based on the chlorine, which is Aschan's 2,6-dichlorocamphane (cf Report 1). Fractionation of the liquid yields unsaturated di- and trichlorides, which were not subjected to further investigation. Their recovery indicates that even under our conditions it is impossible to prevent entirely the further action of the chlorine upon the unsaturated monochloride, or to secure it with a theoretical yield.

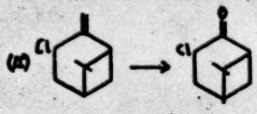
When the pressure is reduced to 1-2 mm, and the reaction product is fractionated at flask temperatures that do not exceed 70°, the picture changes sharply: no hydrogen chloride is evolved, no p-cymene is formed, and more of the monochloride fraction is recovered than in the first case; the quantity of the solid dichloride and the liquid polychlorides is the same as in the first case. The monochloride is nonhomogeneous, and it can be divided into fractions with stable boiling points (45-47° and 55-57° at 2 mm) by fractionation into a tower. The low-boiling fraction is pinocarveol chloride (II), and the high-boiling fraction is myrtenyl chloride (I). The output of the chloride (II) is at least 60% of the total weight of the monochlorides. From this fact we may draw the following conclusions: 1) there is no foundation for the hypothesis that the dichlorides are decomposed as an explanation of the formation of the unsaturated monochlorides, and this hypothesis is incorrect (Lvov); 2) nor is it possible to explain the formation of p-cymene during the chlorination of α-pinene by the decomposition of the dichloride formed as an intermediate (Naudin, cf Report 1); 3) the p-cymene is formed at a higher temperature during the allyl rearrangement of the chloride (I) into the chloride (II) and at its expense, possibly as follows:



4) the primary products of the action of chlorine upon α-pinene are the pinocarveol chloride (II) and Aschan's saturated chloride, the myrtenyl chloride (I) being a secondary product of the allyl rearrangement of the chloride (II). The structure of the chlorides (I) and (II) has been proved by ozonizing them and oxidizing them with potassium permanganate. Oxidation of the chloride (I) yielded a substance with the formula $C_{10}H_{15}ClO_2$ and pinic acid, $C_9H_{14}O_4$, as follows:



which fully proves the structure of (I). The substance with the formula $C_{10}H_{15}ClO_2$ was also synthesized during the ozonolysis of this chloride. Ozonolysis of chloride (II) yielded a substance with the composition of $C_8H_{13}OCl$, and the presence of a carbonyl group in this substance was proved by the synthesis of the semicarbazone, which is possible only if Structure (II) applies:

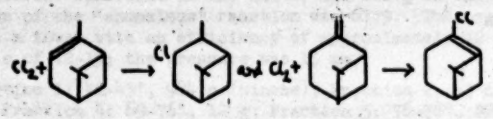


Inasmuch as the chloride (II) is transformed into the chloride (I) by an allyl rearrangement, this very fact proves that a cyclobutane ring is also present in the chloride (II) and finally demonstrates its structure as pinocarveol chloride.

Chlorine was reacted with the β-pinene under the conditions set forth above. Bearing in mind the reports of the allyl rearrangement of α-pinene monochloride, we then and there drove off the excess β-pinene and the monochloride fraction from a Würtz flask at a pressure of 1 mm and a bath temperature no higher than 70°. Subsequent fractionation of the monochlorides into a tower was effected at the same pressure. Only one monochloride fraction was secured. Its constants agreed with the constants of the chloride (I). Its ozonolysis yielded only a substance with the composition of $C_{10}H_{15}ClO_2$; no chloroketone with the composition $C_9H_{13}OCl$ was secured. Thus, the action of chlorine upon β-pinene yielded the monochloride (I) (myrtenyl chloride) and the dichloride, which entails a shift of the double bond according to our scheme. It has been shown above that the chloride (II) is irreversibly rearranged into the chloride (I) at 70°, and that it is stable below 70°. Inasmuch as the production of the monochlorides of β-pinene has been effected at a lower temperature than 70°, there is no reason to consider the chloride (I) as a secondary product in this case. The higher-boiling residue did not crystallize as it had in the case of α-pinene. In a separate paper we shall report that the saturated dichloride of Δ^3-carene is also a liquid. This proves that the preconceived notion that terpene dichlorides must be crystalline (cf Report 1) is incorrect.

Thus, the action of chlorine upon α-pinene yielded pinocarveol chloride with a shifted double bond and the saturated dichloride as intermediate products, while the action of chlorine upon β-pinene yielded myrtenyl chloride with a shifted double bond and a dichloride, which fully refutes both the the "substituent" schemes of olefin chlorination put forward by American researchers and corroborates our scheme entirely.

Report 1 sets forth a number of considerations that enable one to judge, from our point of view, the hypothetical structure of terpene monochlorides formed by the reaction of chlorine with terpenes, as well as their stability. The results we have achieved bear out these considerations: the double bond does not shift to the cyclobutane ring as follows:



constituting systems that would be under considerable stereochemical stress; the chloride (II) is unstable and is isomerized to the chloride (I) when heated (the instability of compounds with a semicyclic double bond).

In the case of α-pinene, the "anomalous" reaction represents 65-67% of the total, with the "classic" one accounting for 35-33%; in the case of β-pinene, the respective figures are 50-52% and 50-48%, which agrees with our previous concepts of the greater or lesser "proton similarity" of the hydrogen atoms in the methyl and methylene groups (cf Report 1). The proportion of the reactions was computed as follows: in the "anomalous" reaction, half the chlorine is converted into hydrogen chloride, the other half entering into the monochloride; in the "classic" reaction, all the chlorine enters into the composition of the dichloride. Multiplying the amount of the mineralized chlorine by two, dividing by the amount of chlorine consumed, and multiplying the fraction by 100 gives the percentage of the "anomalous" reaction.

In the chlorination of α- and β-pinenes and of all the others we have investigated, the amount of the monochloroterpene recovered is lower than what should be expected from the proportion of the "anomalous" reaction. The fundamental reason for this discrepancy is the reaction of the monochloroterpenes with chlorine, resulting in the formation of unsaturated dichlorides and polychlorides (cf the experimental section below). To prevent this, a much larger excess of the original terpene should be employed than we used.

EXPERIMENTAL

The Reaction of Chlorine with α-Pinene

The α-pinene was prepared by doubly distilling turpentine oil. The efficiency of the tower was about 12 theoretical trays, and the reflux ratio was 12-15. A fraction with a b.p. of 52-52.5° at 20 mm; d_4^{22} 0.858; n_D^{22} 1.4684, was collected.

α-Pinene and sodium bicarbonate (the latter in 100% excess over what is required to bind the HCl) were placed in a flask fitted with a powerful stirrer. The chlorine was produced by pouring strong hydrochloric acid upon a weighed quantity of $KMnO_4$; then it was washed with water, desiccated with H_2SO_4, and stored in a tank that was chilled with snow and salt, at such a rate that the temperature in the tank did not rise above -3 to -5°. A wash bottle filled with water was set up at the outlet to check on the evolution of CO_2 and to absorb any traces of HCl. The speed of the stirrer was regulated by means of a rheostat so as to effect complete suspension of the $NaHCO_3$. The amount of chlorine added was half the molar concentration of the pinene. After the reaction was complete, the salts were filtered out by suction, and washed with ether; the ether was eliminated from the wash liquid, and the residue was added to the filtrate. The salts were dissolved in water, and the percentage of chlorine ions ("mineralized" chlorine) in the solution was determined quantitatively. The organic portion was

was weighed, and its chlorine content was determined by the Carius method ("organic" chlorine).

Experiment 1. 1630 g (12 mols) of the pinene, 600 g of $NaHCO_3$, and 385 g of chlorine (5.5 mol, on the basis of 350 g of $KMnO_4$). After the reaction was over, 108 g of chlorine was found in the salts, and 210 g in the organic portion, and the percentage of the "anomalous" reaction was 67.9. The organic portion was fractionated into a tower with an efficiency of approximately 12 theoretical trays and a reflux ratio of 12-15; the pressure was 13 mm.

Yield: Fraction 1: 42-43°, 984 g (pinene); Fraction 2: 43-67°, 4 g; Fraction 3: 67-69°, 85 g; Fraction 4: 69-76°, 12 g; Fraction 5: 76-78°, 28 g; Fraction 6: 78-87°, 8 g; Fraction 7: 87-89°, 310 g; Fraction 8; 89-100°, 32 g; Fraction 9; 100-130°, 50 g; and a residue of 54 g.

After the pinene had been distilled, the pressure in the system was observed to rise sharply and hydrogen chloride was evolved; no more was collected until the original pressure had been restored. After Fraction 7 had been distilled, the contents of the flask crystallized all at once; the crystals were filtered out by suction (168 g), and the liquid was returned to the flask.

Analysis of the fractions. Fraction 3: d_4^{16} 0.8582, traces of chlorine. The 85 g was agitated with 100 ml of H_2SO_4 (sp. gr. 1.69) in order to eliminate the terpenes. The hydrocarbon layer was separated, distilled with steam, and desiccated. All of it passed over at 177.5-178°; d_4^{22} 0.867; n_D^{22} 1.4897, when distilled into a small tower. This in in good agreement with the constants of p-cymene. The substance was oxidized by boiling it with an alkaline solution of permanganate. This yielded an acid with a m.p. of 155-155.5° and an equivalent of 179, which corresponds to p-hydroxyisopropylbenzoic acid.

Fractions 4, 5 (d_4^{16} 0.966, 12.4% Cl), and 6 were not analyzed.

Fraction 7: b.p. 87-89° at 13 mm, %Cl = 19.9 and 20.0; d_4^{16} 1.0095; n_D^{20} 1.4976, MR_D found for $C_{10}H_{15}Cl$ was 49.0, and computed for $C_{10}H_{15}Cl$ $\overline{f}$. was 48.8. A weighed quantity of the fraction was heated for 30 minutes with alcoholic alkali; the Cl' was titrated back, and the active allylic chlorine was found to be 19.9 and 19.9%.

Oxidation of the monochloride in acetone. This experiment was repeated three times, each time 51 g of the chloride being oxidized. A 4% solution of permanganate (128 g) was added, with stirring, to the acetone solution of the chloride. In a second test, 20 g of glacial acetic acid was added to the original acetone solution, and 60 g of the acid was added in a third test. After oxidation was complete, the manganese dioxide was filtered out by suction and washed repeatedly with water. The water extract was greatly reduced, acidulated, and extracted with ether, the ether was driven off from the extract, and the residue was distilled. Almost all the substance passed over at 184-186° at 4 mm; it was a viscous liquid. Analysis: the per cent carbon was found to be 58.4 and 58.2; the per cent hydrogen was found to be 7.8 and 7.7; the computed figures for $C_9H_{14}O_4$ are 58.1 and 7.5%, respectively. A silver salt that is fairly soluble in water was produced. Analysis: % C = 26.9 and 26.8; % H = 3.3 and 3.4; % Ag = 54.7 and 54.8; $C_9H_{12}O_4Ag_2$ corresponds to 27.0, 3.0, and 54.0%, respectively. Hence, the resulting acid is pinic acid.

The solvent was eliminated from the acetone solution and the residue was fractionated. In all three experiments, two fractions with stable boiling points were secured: an 82-84° fraction at 9 mm, d_4^{20} 1.009 (the initial monochloride); and a 119-120° fraction at 3 mm, d_4^{20} 1.188, n_D^{20} 1.5086. Analysis: % C = 59.7 and 59.7; % H = 7.7 and 7.6; % Cl = 17.8 and 17.5. The respective percentages for $C_{10}H_{15}ClO_2$ are computed as % C = 59.4; % H = 7.4; and % Cl = 17.5.

Three experiments yielded the following quantities of the foregoing substances:

	Original monochloride	$C_{10}H_{15}ClO_2$	$C_9H_{14}O_4$
1.	18.0 g	6.5 g	9.0 g
2.	7.5 g	11.0 g	6.0 g
3.	5.0 g	29.0 g	2.0 g

Investigation of the crystalline product of the chlorination of α-pinene. A constant m.p. of 173-174° was attained after triple crystallization from light gasoline; % Cl = 34.4 and 34.5; the molecular weight was found to be 208.0 and 208.5; the respective figures for $C_{10}H_{16}Cl_2$ are computed as 34.3 and 207. The substance is evidently Aschan's 2,6-dichlorocamphane (cf Report 1).

Experiment 2. We used 544 g of α-pinene, 175 g of chlorine (computed from the $KMnO_4$), and 300 g of $NaHCO_3$. The chlorination conditinns were the same as before. Most of the excess pinene was first driven off from the reaction mixture at 7 mm (bath temperature no higher than 50°), after which fractionation was continued from a Würtz flask at 1 mm pressure, yielding:

Fraction No.	Boiling point	Bath temperature	Weight, g	
1.....	to 42°	50°	120	
2.....	42	50	180	
3.....	42-50	60	115	
4.....	52-62	70	31	
5.....	62-85	100	26	solidified in condenser
Residue	.....	.....	138	solidified

No hydrogen chloride was evolved during this distillation or the subsequent rectification. The monochloride fractions 2, 3, and 4 were fractionated into a tower with an efficiency of 4 theoretical trays and a reflux ratio of 10. The bulk of the monochloride boiled at 44-47° and 1 mm (170 g). Ozonolysis of this fraction demonstrated its heterogeneity. A chloroketone with the composition of $C_9H_{13}OCl$ and the substance $C_{10}H_{15}O_2Cl$ (cf Experiment 3) were recovered, and we therefore set up a third chlorination test involving fractionation of the monochlorides into a specially designed, more effective tower. Crystals were separated by suction from the high-boiling residue of the second test (103 g, 21% of the theoretical chlorine yield), while the liquid portion was distilled at 0.5 mm.

Yield: Fraction 1: 15 g at 60-95°, d_4^{22} 1.111; % Cl = 34.5; M = 196; % Cl = = 34.6 and M = 205 for $C_{10}H_{14}Cl_2$.

Fraction 2: 16 g at 95-110°, d_4^{22} 1.150; % Cl 37.6; M 211; % Cl = 34.6 and M = 205 for $C_{10}H_{14}Cl_2$.

Fraction 3: 12 g at 110-140°, d_4^{22} 1.236; % Cl = 42.4; M = 228; % Cl = 44.6 and M = 240 for $C_{10}H_{13}Cl_3$.

All of these fractions decolorize bromine in chloroform.

Experiment 3. The quantities of substances and the conditions were the same as in Experiment 2. The excess pinene and the monochloride fractions (b.p. 42-62°, 330 g) were distilled from a Würtz flask at 1 mm. The monochloride fractions were twice fractionated into a tower with an efficiency of 8 theoretical trays, with regulated heating and complete condensation of the vapors, the reflux ratio being 12-14 and the pressure being 2 mm. Subjoined are the data of the last fractionation:

Fraction No.	Boiling point	Weight, grams
1	45 - 47.5	86.3
2	47.5-50	15.9
3	50 - 53	5.7
4	53 - 55	12.1
5	55 - 57.5	60.9
6	57.5-59	6.4
Residue.....		29.1

Fractions 1 and 5 were analyzed.

Analysis of Fraction 1 (45-47.5° at 2 mm); d_4^{22} 1.016; n_D^{22} 1.14984; % Cl = = 20.70 and 20.65; M = 167 and 169; the % Cl was computed to be 20.8 and the M 170.5 for $C_{10}H_{15}Cl$. 22 g of the chloride in 70 g of chloroform chilled to -70° was saturated with 90 liters of 5% ozone (15% excess). The solution of the ozonide was dropped into boiling water containing platinum black (to decompose the H_2O_2), and the chloroform, water, and the ozonlysis products were collected in a receiver chilled to -23°. The undistilled residue weighed 4.5 g. The water and chloroform solutions were separated and analyzed.

The water layer was reduced to 1 liter. The reaction with a solution of Schiff's reagent in 0.1 N HCl was positive (formaldehyde). 20 ml of the solution was precipitated with dimedon. The precipitate weighed 0.1188 g; its m.p. was 189°; the total amount of CH_2O in solution was 0.604.

The chloroform was driven out of the chloroform solution, and the residue was fractionated at 0.5 mm.

Yield: Fraction 1: 3.4 g at 65-67°; Fraction 2: 2.1 g at 77-78.5°; Fraction 3: 1.1 g at 78.5-95°; residue is 9 g.

The 65-67° fraction had d_4^{22} 1.030; n_D^{22} 1.4900; % Cl = 20.14 and 20.28; % C = 62.3 and 62.9; % H = 7.6 and 7.7; M = 169.7 and 170.4; the percentages computed for $C_9H_{13}OCl$ are: % Cl 20.6; % C 62.7; % H 7.5; M = 172.5.

When kept with semicarbazide acetate in a water-alcohol solution for 10 days, the substance formed a precipitate of yellow crystals of the semicarbazone, which fused at 223-225°.

The 77-78.5° fraction had d_4^{22} 1.1558, n_D^{22} 1.5010; its analysis showed: % Cl = 17.4 and 17.4; % C = 59.5 and 59.9; % H = 7.7 and 7.6; M = 203 and 204; the percentages computed for $C_{10}H_{15}O_2Cl$ are: % Cl = 17.5; % C = 59.3; % H = 7.4; M = 202.5.

Analysis of Fraction 5 (55-57° at 2 mm; d_4^{22} 1.013; n_D^{22} 1.4952; % Cl 20.9 and 20.9.

Ozonation. 18 g of the chloride was thoroughly ozonized, as set forth above. Subsequent treatment was the same as above. No formaldehyde was found in the aqueous layer. Fractionation of the chloroform layer (0.5 mm pressure) yielded: 5.1 g of Fraction 1 at 78-80°; 0.9 g of Fraction 2 at 80-96°; and a residue of 7.8 g. None of the chloroketone $C_9H_{13}OCl$ with a b.p. of 65-67° was secured. The constants of Fraction 1 were: d_4^{22} 1.160; n_D^{22} 1.5052; % Cl 17.3 and 17.4; % C 60.0 and 60.3; % H 7.4 and 7.4; M = 204 and 205. The percentages computed for $C_{10}H_{15}O_2Cl$ are: % Cl 17.5; % C 59.3; % H 7.4; M = 202.5.

Reaction of Chlorine with β-Pinene

The β-pinene was synthesized by the double fractionation (into a tower with 12 theoretical trays and a reflux ratio of 15-16) of the β-pinene fraction of turpentine oil produced by the Barnaul plant [11]. The collected fraction had the

following constants: b.p. 59-60° at 20 mm; d_4^{22} 0.8705; n_D^{22} 1.4789; $[\alpha]_D^{15}$ -11.86°; which agree with the constants for β-pinene [12] with the exception of the specific rotatory power (≈-20°). The latter discrepancy may be due to the racemization of the β-pinene during the prolonged industrial rectification of the turpentine at atmospheric pressure, which is required to isolate the small quantities of β-pinene fraction (our turpentines contain 6-8% β-pinene). To prove that the recovered fraction was identical with β-pinene, 15 g of the fraction was oxidized with 35 g of $KMnO_4$ in 450 ml of an aqueous alkaline solution (7.5 g of NaOH). This yielded 1.1 g of sodium nopinate (7% by weight), i.e., the normal quantity for pure β-pinene [13].

Chlorination of the β-pinene was effected under the conditions set forth above. 544 g of β-pinene, 175 g of chlorine (based on 160 g of $KMnO_4$) and 300 g of $NaHCO_3$ were used in the reaction. 44.7 g of Cl was found in the solution of mineral salts. 127.8 g of chlorine was found in the organic products. The "anomalous" reaction represented 51.8% of the total. The organic portion was first distilled from a Würtz flask at 1 mm and a bath temperature no higher than 70°. The residue did not crystallize.

The monochloride fractions (collected by sp. gr. and refractive index) were twice fractionated into the above described tower with a rating of 8 theoretical trays at 0.5 mm. The data for the last fractionation were as follows: 4.3 g of Fraction 1 at 28-34°; 14.2 g of Fraction 2 at 34-39°; 152.7 g of Fraction 3 at 39-42°; 30.0 g of Fraction 4 at 42-44°; and 4 g of a residue. The following values were found for Fraction 2: %Cl = 9.2 and 9.3; M = 149 and 153. The following values were found for Fraction 3: d_4^{22} 1.017; n_D^{22} 1.4954; % Cl = 20.9 and 20.6; M = 168 and 170; the values computed for $C_{10}H_{15}Cl$ are: % Cl 20.8; M 170.5. The following values were found for Fraction 4: % Cl = 21.2 and 21.6; M 174 and 176.

Ozonating Fraction 3. 25 g of the fraction was saturated with 100 liters of 5% ozone under the conditions set forth above. Cf the foregoing for the further treatment. No formaldehyde was found in the aqueous layer. Fractionation of the chloroform layer (1 mm pressure) yielded: 6.2 g of Fraction 1 at 86-88°; 0.4 g of Fraction 2 at 88-95°; and 10 g of a residue. The data for Fraction 1: d_4^{22} 1.151; n_D^{22} 1.5010; % Cl = 17.6 and 17.6; % C = 59.8 and 59.6; % H = 7.4 and 7.4; M = 202 and 206. The values computed for $C_{10}H_{15}O_2Cl$ are: % Cl = 17.5; % = 59.3; % H = 7.4; and M = 202.5.

SUMMARY

1. The action of chlorine upon α- and β-pinenes has been used as an example to test the theoretical concepts set forth in our Report I.

2. Pinocarveol chloride (main reaction) and the saturated dichloride (side reaction) are the primary products of the action of chlorine upon α-pinene, while myrtenyl chloride (main reaction) and a dichloride are the primary products in the case of β-pinene.

3. It has been shown that all previous investigations of this problem are worthless because of their erroneous theoretical notions of the way in which chlorine reacts with the α- and β-pinenes and their experimental errors.

4. It has been established that the conclusions of our Report I are in accordance with reality and the analogy of the terpenes with the quaternary olefins in their reactions with chlorine has been demonstrated.

5. The incorrectness of the theory of "substituent" chlorination has been confirmed, using the terpenes as examples.

6. It has been shown that the chlorohydrin of pinocarveol is irreversibly

isomerized to the chlorohydrin of myrtenol at temperatures above 70°, in accordance with the conclusions of our Report I.

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* See CB translation p. 598 ff.

NEW TYPES OF TERPENE TRANSFORMATIONS

III. THE ACTION OF CHLORINE UPON DIPENTENE

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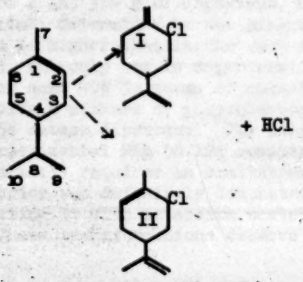
In our first report [1] we set forth our notions of the possible general mechanism of the action of chlorine upon the terpenes. There is no reference in the chemical literature to the action of chlorine upon dipentene and limonene, so that in this instance the correctness of our concepts can be checked only by experiment. According to the concepts set forth previously [1], in dipentene the Δ^1 double bond ought to react much faster with chlorine than does the $\Delta^{8,9}$ double bond (the Δ^1 double bond is more highly branched).

Chlorine may react with the Δ^1 double bond in two possible ways.



The synthesis of the chloride (I) is less likely thermodynamically, inasmuch as the formation of the semicyclic $\Delta^{1,7}$ double bond requires an energy consumption of the order of 6-8 cal per mol (cf Report I). Hence, much more likely is the formation of the chloride (II), carveol chloride, with the double bond shifted to the 1,6-position, which is equivalent to the 1,2 position, owing to freedom of rotation about the 4,8 bond. Thus the chloride (I) might be taken, (formally speaking) as the product of the "substituent" chlorination advocated by the American school (cf Report II [2]), but this conclusion is unfounded: even Hass's "α-substituent" scheme provides for the formation of three chlorodipentenes (with chlorine atoms at the 3, 6, and 7 positions), whereas the "substituent" scheme in its general form calls for at least six chlorodipentenes (chlorine atoms at the 3, 4, 5, 6, 7, and 10 positions). Thus this case enables us, once again, to check whether the mechanisms for the chlorination of olefins that are branched at a double bond previously considered (Report II) conform to reality, and to

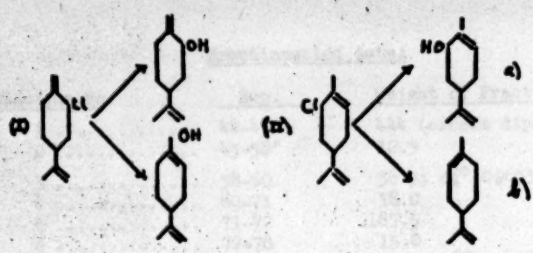
select the correct one.

Report II sets forth the results of the action of chlorine upon α- and β-pinenes, which are bycyclic terpenes with one double bond. The primary products of their reaction with chlorine are the chlorohydrins of pinocarveol and myrtenol, respectively. In these chlorohydrins the chlorine atoms are attached to the radicals that are linked to the more highly branched ends of the double bonds, which must involve the depolarization of the double bond and a lower velocity of its reaction with chlorine, compared to that for the original terpene [3]. Despite this, these monochlorides, as they accumulate in the reaction medium, do begin to react with the chlorine, together with the terpene, yielding unsaturated dichlorides and polychlorides, which results in a decrease in the output of the monochlorides.

In the case of dipentene, this decrease ought to be even more marked, inasmuch as the monochloride (II) has two double bonds, each of them able to react with chlorine according to our scheme: we should expect that the analytical determination of the output of the "anomalous" reaction (cf Report II) will be even farther from the actual yield of the monochloride (II) than was the case with the α- and β-pinenes. We might combat this phenomenon by diminishing the quantity of chlorine employed in the reaction (using a large excess of terpene), but it has not been our objective to elaborate the technically optimum procedures for synthesizing the terpene monochlorides; we have endeavored rather to discover the underlying mechanism of the action of chlorine upon the terpenes under comparable conditions, and we therefore always employed the same terpene: chlorine ratio of 2:1 (cf Reports II, III, et seq).

Chlorine was reacted with dipentene under the conditions set forth in Report II. Two tests were run with 888 g and 334 g of dipentene, respectively. The yields of the "anomalous" reaction, determined by the mineralized chlorine, were 86 and 88%, respectively, which is higher than in the case of α-pinene (there are two "interdictions" in α-pinene, but only one in dipentene). Fractionation yielded a monochloride, with yield of some 40% in terms of chlorine, which boiled within a range of one degree, plus a mixture of polychlorides that boiled over a wide range, in addition to the excess dipentene. The molecular refraction of the monochloride was normal: experimental MR_D 50.12; computed for $C_{10}H_{15}ClF_2$, structure (II), 50.11. Structure (I) requires an exaltation of the order of 0.3-0.4. The structure of the chloride was definitely demonstrated by converting it into carveol acetate by reacting it with potassium acetate, isolating the carveol, and identifying it. These transformations deserve a preliminary consideration.

We know that the saponification of allyl chloride is a monomolecular reaction. Subsequently, it was discovered that the same held true for 2-chloromethyl--3-chloropropene-1 [5]. Moreover, it is common knowledge that an allyl rearrangement may occur in the anion exchange reactions of allylic halides. In the conversion of the chloride (II) into carveol acetate outlined above we used aqueous acetic acid and obtained an acetate with traces of an alcohol. As will be reported in a special paper, anion exchange reactions of the terpene monochlorides yield terpene derivatives of all the anions present in the solution. Hence, if we want to secure the maximum yield of a single product, the solution should contain only one anion (in the given case, potassium acetate and anhydrous acetic acid). Such behavior of the chloride (II) is fully compatible with its structure as a homolog of allyl chloride, and it enables us to establish its structure by converting it into carveol: all the chlorine in the chloride is active and quickly reacts when boiled in alcoholic or acetic solutions with various reagents; hence, it is allylic [6]; when we examine the saponification of the chlorides (I) and (II), it is not difficult to see that carveol can be produced only from the chloride (II):



Structures a and b are equivalent, owing to freedom of rotation about the 4-8 bond.

The carveol was produced with an excellent yield and high purity. The chloride (II) yielded a carveol of a high yield and purity, which gave nearly quantitative yields of crystalline derivatives, phenylurethane, and an acid phthalate. This method of preparation makes it a readily available substance, inasmuch as dipentene may be produced by the thermal isomerization of α-pinene, by the Arbuzov method, the ensuing operations being simple and inexpensive. Up to the present time, the sole source of dipentene has been caraway oil. The procedure for recovering it from this oil is rather complicated and expensive. The autoxidation of dipentene cannot be considered a satisfactory method of preparing carveol (cf Report I); the Genwresse method (reacting nitrogen oxides with dipentene) [7] is even less satisfactory.

The outlined method of synthesizing carveol from dipentene via the monochloride is of great importance in principle. It is the first realization of our general method for the synthesis of terpene derivatives with the same degree of saturation and the same carbon skeleton as in the original terpenes via the monochlorides of the terpenes. It paves the way for a series of researches, projected by us and already carried out to some extent.

The high purity of the synthesized carveol is proof of the purity of the original chloride and of the absence of other, isomeric chlorides in it, which once more refutes the notion of "α-substituent" chlorination. The carveol was oxidized to carvone by chromic anhydride, with a satisfactory yield. The resultant carvone was homogeneous, both physically and chemically, possesses the constants that are characteristic of this compound, and yields a characteristic oxime and hydrogen-sulfide derivative, which again testifies to the purity of the synthesized carveol.

EXPERIMENTAL

The dipentene was prepared by thermally isomerizing α-pinene [8] and was isolated by fractionation into a tower with a rating of 20 theoretical trays. B.p. 72° at 20 mm; d_4^{20} 0.8436.

Chlorination was carried out under the conditions set forth previously [2]. The yield of the "anomalous" reaction was 86-88%. We reproduce the data for a single run below: 880 g of dipentene, with 255 g of chlorine consumed, 114 g being found in the salts, and 141 g in the organic products. Theoretically, 548 g of the monochloride should be produced. A total of 1008 g was fractionated (13 g of dipentene was lost in chlorination, owing to its being entrained by carbon dioxide). Fractionation was carried out with a tower rated at about 7-8 theoretical trays at a reflux ratio of 10 and a pressure of 3 mm. The data for the first fractionation run are given below:

Subsequent fractionation of the monochloride Fraction Nos. 3-8 into a tower of the same rating, but at a reflux ratio of 15-17 and a pressure of 0.35 mm in the receiver, yielded a single monochloride fraction with a b.p. of 57-58°,

Fractionation data:

Fraction No.	B.p.	Weight of Fraction, grams
1	44-45°	444 (excess dipentene)
2	45-58°	12.5
3	58-60	38.5; d_4^{20} 09653 ; n_D^{20} 1.5034; % Cl 16.5
4	60-71	18.0
5	71-72	187.5
6	72-78	15.0
7	78-80	60.0; n_D^{20} 1.4987; % Cl 24.3, 24.4.
8	80-90	8.0
9	90-100	15.5 d_4^{20} 1.077.
10	100-110	19.5 d_4^{20} 1.139.
11	110-130	6.0
12	130-150	52.0; d_4^{20} 1.146; n_D^{20} 1.5166;
.....	Residue	71.5 % Cl: 34.5, 34.5.
	Losses	60.0. Total, 1008.0.

d_4^{20} 1.009; n_D^{20} 1.49925; the monochloride fractions that boiled above and below this interval totaled 12 g. The large quantity of high boiling fractions (164.5 g) despite the high proportion (88%) of the "anomalous" reaction is worthy of note as an indication of the extent of the reaction between the monochloride and the chlorine.

Analysis of Fraction 5

d_4^{20} 0.9998; n_D^{20} 1.49805; MR_D found 51.2; computed 50.11; % Cl 20.3, 20.5; % allylic chlorine 19.8, 19.9; $C_{10}H_{15}Cl$ computed 20.8% Cl.

85 g of the chloride, 50 g of potash, and 200 g of 96% acetic acid were heated to boiling for 2 hours. 31.5 g of potassium chloride settled out (84% of the theoretical yield). The acetic acid was driven off in vacuum with a dephlegmator; the residue was diluted with water and twice extracted with ether, the ether was driven off, and the residue was fractionated at 4 mm into a tower rated at 6-8 theoretical trays.

Yield: 1) 7 g up to 70°; 2) 10 g at 70-99°; 3) 54 g at 99-101°; 4) 4 g at 101-120°; 6 g of residue. 1) exhibits a reaction for chloro derivatives; 2) exhibits a reaction for alcohols (evolves hydrogen with Na and evolves methane with CH_3MgI); 3) has a n_D^{20} 1.47785 and a saponification number of 286, the computed number for $C_{10}H_{15}OCOCH_3$ being 288. 53 g of the acetate was saponified by boiling it for six hours with an excess of alcoholic alkali. The alcohol was driven off, the residue was diluted with water and extracted with ether, and the ether was driven off. The residue weighed 44 g. All of it distilled at 129° and 28 mm; d_4^{20} 0.9524; n_D^{20} 1.49625; the MR_D for $C_{10}H_{15}OH$ was found to be 46.63; its computed value was 46.77. Analysis: % C 78.9 and 78.7; % H 10.4 and 10.4; the respective computed values for $C_{10}H_{15}OH$ are 78.9 and 10.5%. The experimental constants agree with those of dl-carveol.

The synthesized alcohol does not react with phthalic anhydride in boiling benzene, but it does react when fused with it at 125° and hence is a secondary alcohol [10], which produces a nearly quantitative yield of the acid phthalate, which fuses at 136-136.5° after a single recrystallization from gasoline. Subsequent crystallizations do not change the melting point; the acid phthalate of dl-carveol fuses in the same manner [9]. 0.5 g of the alcohol and 0.5 g of phenyl isocyanate were placed in a sealed ampoule and heated over a boiling bath for one hour. All the contents of the ampoule solidified after three weeks. The phenylurethane fuses at 94-95° after a single recrystallization from gasoline, as is the case with the phenylurethane of dl-carveol, [9]. Subsequent recrystallization

has no effect upon the melting point.

Oxidation of dl-carveol. 14 g of chromic anhydride in 200 ml of acetic acid was added, with constant stirring and chilling with ice, to 30 g of alcohol in 100 ml of acetic acid. The reaction product was diluted to one liter and blown off with steam. 22 g of an oil with the odor of fennel was recovered by fractionation into a tower with a herringbone packing at a pressure of 27 mm. Yield: 1) 2 g up to 124°; 2) 17.5 g at 124-126°; d_4^{20} 0.9588; n_D^{20} 1.4948; MR_D found for the ketone $C_{10}H_{14}OF_2$ was 45.60; the computed value is 45.28; the magnitude of the exaltation was characteristic of carvone. The oxime was prepared as specified by Wallach [4]; it fused at 92-93° after recrystallization from aqueous alcohol, as does the oxime of dl-carvone [9]. Analysis: % N 8.4 and 8.4; the computed value for $C_{10}H_{15}ON$ is 8.48%. 2 g of the ketone + 1 g of alcohol + 0.5 g of aqueous ammonia [illegible]e saturated with hydrogen sulfide. Crystallization sets in almost immediate[illegible]. The crystals were recovered by suction and recrystallized three times from ethanol until their m.p. was constant at 189-190°, which is the m.p. of the hydrogen-sulfide derivative of dl-carvone.

SUMMARY

1. A study has been made of the reaction of dipentene with chlorine under conditions that ensure the recovery of the primary reaction products.

2. The primary reaction product is 6-chlorodipentene (carveol chloride), which conforms to our proposed scheme for the reaction of chlorine with branched olefins and refutes the "substituent" scheme of the American school [2]. The structural peculiarities of dipentene had led us to fortell the production of this very chloride of carveol.

3. It has been shown that carveol chloride may be transformed, with satisfactory yield, into a carveol of high purity; this is the first satisfactory synthesis of carveol from dipentene. Moreover, this synthesis is the initial example of a general method we have developed for synthesizing terpene derivatives with the same degree of saturation and the same carbon skeleton as the original terpene.

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THE REACTION OF HETEROCYCLIC AMINES WITH UREA

I. THE REACTION OF SOME AMINO DERIVATIVES OF PYRIDINE WITH UREA

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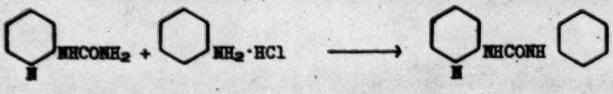
Little work has been done on the reaction of the heterocyclic amines with urea. We proposed to make a study of the reaction of urea with some amines of the pyridine series. Our researches started with a study of the reaction of 2-aminopyridine with urea. There is a statement in the literature to the effect that Schmid and Becker [1] had synthesized a substance to which they ascribed the structure of N,N'-di(pyridyl-2)-urea, by heating 2-aminopyridine with urea. Our studies have demonstrated that the data given by Schmid and Becker are wrong. We obtained the following results when we condensed 2-aminopyridine with urea.

When α-aminopyridine was heated with urea for 5 hours at 150°, a crude product was recovered from the reaction, from which, in turn, we were able to isolate two different individual substances, depending on the solvent employed for crystallization; the structure of these substances was determined only after very long research. Crystallization of the crude product from pyridine or alcohol yielded a product with a m.p. of 155-156.5°, the melting point of which was unaffected by further crystallization. When the crude product was crystallized from water, we got a different product, with a m.p. of 173°.

When the substance with a m.p. of 155-156.5 was crystallized from water or was agitated with an alkaline solution, it was converted into the substance with a m.p. of 173°, urea being found in the mother liquor.

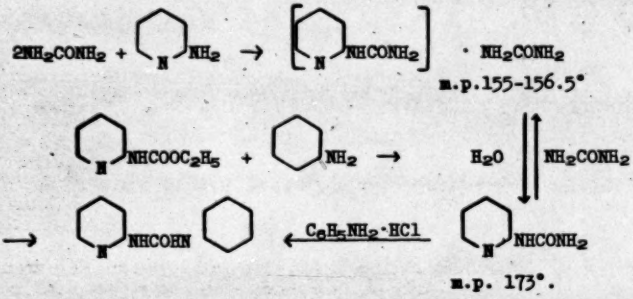
All these facts indicated that the substance with a m.p. of 155-156.5° is an unstable molecular compound of urea with the substance with a m.p. of 173°. Analysis of the two substances bore out our assumption. The substance with a m.p. of 173° had the composition of $(C_5H_4N)NHCONH_2$; the substance with a m.p. of 155-156.5° was the compound $[(C_5H_4N)NHCONH_2]\cdot NH_2CONH_2$.

Our first job was to demonstrate the structure of the substance with a m.p. of 173°. Despite the fact that the synthesis process and the analysis of the substance indisputably indicated that we were dealing with α-pyridylurea, we still felt it was necessary to perform special research in order to prove the structure of the substance with a m.p. of 173°. This was due to the fact that our product exhibited a depression when mixed in a test sample with the substance secured by O.Fischer [2] when he heated α-aminopyridine with potassium cyanate, to which he gave the structure of N-(pyridyl-2)-urea. We proved the structure of our substance: 1) by heating it with aniline hydrochloride to produce N-(phenyl)-N'-(pyridyl)-urea:



which is identical with the substance synthesized by Camps [3] by heating (pyridyl-2)-urethane with aniline; and 2) by saponifying it with an alkali solution to yield α-aminopyridine. We finally demonstrated the structure of the substance with a m.p. of 155-156.5° by producing it by heating urea with the substance with a m.p. of 173° [i.e., N-(pyridyl-2)-urea].

We thus proved that heating α-aminopyridine with urea yielded the molecular compound of N-(pyridyl-2)-urea with urea, which breaks down when heated into N-(pyridyl-2)-urea and urea:



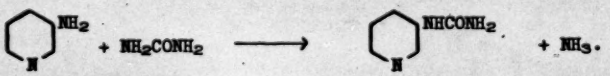
The assertions of Schmid and Becker that heating α-aminopyridine with urea at 180° yielded N,N'-di-(pyridyl-2) urea were found to be erroneous. When we repeated the Schmid and Becker experiment, we did not secure N,N'-di-(pyridyl-2)-urea.

We then had to settle the question of what the substance was that is secured when an aqueous solution of α-aminopyridine is boiled with potassium cyanate, to which O. Fischer assigned the structure of N-(pyridyl-2)-urea. To do this, we repeated the experiment described by O. Fischer. For a long time we secured nothing but α-aminopyridine and inorganic salts in these tests. But in one of the tests, when we employed freshly prepared potassium cyanate, we obtained a substance with a m.p. of 175°, which exhibited a depression with the N-(pyridyl-2)-urea we had synthesized. Our analysis for C, H, and N showed that the substance answered to the composition of α-pyridylbiuret. The error in O. Fischer's conclusions lies in the fact that he based them solely upon an analysis for nitrogen, whereas the percentage of nitrogen is nearly the same for pyridyl-urea and for α-pyridylbiuret.

We synthesized N,N'-di(pyridyl-2)-urea by reacting phosgene with α-aminopyridine (in the presence of sodium amide, or without it), or by reacting ethyl carbamate with α-aminopyridine. Both of these methods are superior to Camps' method [3] in that they enable the synthesis to be performed in a single stage.

We then wanted to make a study of the reaction of 3-aminopyridine with urea.

When 3-aminopyridine was heated to 160° with urea, we obtained N-(pyridyl-3)-urea:



We found no molecular compound in this reaction, as we had when urea was condensed with 2-aminopyridine.

Our subsequent research had as its objective the study of the reactions of aminonitropyridine and dialkyldiaminopyridine with urea. Our research in this field demonstrated that the nitro group in the 5 position in 2-aminopyridine prevents the condensation reaction with urea. When 2-amino-5-nitropyridine was condensed with urea, we were unable to secure urea derivatives. When 2-dimethylamino-5-aminopyridine was condensed with urea, we obtained N,N'-di-(2-dimethylaminopyridyl-5)-urea.

EXPERIMENTAL

Condensation of α-Aminopyridine with Urea

A mixture of 94 g (1 mol) of purified α-aminopyridine and 30 g (½ mol) of urea was heated over an oil bath for 5 hours. The gas evolved during the reaction was absorbed in 1 N hydrochloric acid. Evaporation of the hydrochloric acid yielded 13.5 g of ammonium chloride (0.25 mol). After the reaction was over, the melted mass was poured into a porcelain dish. The solidified melt was triturated with ether until the odor of α-aminopyridine disappeared. Weight 20 g. M.p. 153° (Substance A). Part of Substance (A) was recrystallized from alcohol, another part from pyridine, and still another part from water.

1. When substance (A) was recrystallized from alcohol – either absolute or 96% (or even from pyridine), acicular crystals with a m.p. of 155-156.5° (Substance B) settled out of the mother liquor. When Substance (B) was heated with an aqueous solution of sodium hydroxide, ammonia was liberated.

2. When Substance (A) was recrystallized from water, colorless prisms with a m.p. of 170-173° (Substance C) settled out of the mother liquor. A sample of this substance mixed with a test sample of N,N'-di-(pyridyl-2)-urea (prepared by Camps' method) exhibited depression of the melting point. The structure of Substance (C) was proved as indicated below.

1) Analysis of Substance (C).

5.303 mg substance: 2.410 mg H_2O; 10.246 mg CO_2.
6.130 mg substance: 2.820 mg H_2O; 11.796 mg CO_2
3.172 mg substance: 0.872 ml N_2 (23°, 734 mm).
3.430 mg substance: 0.948 ml N_2 (23°, 734 mm).
Found %: C 52.69, 52.48; H 5.09, 5.15; N 30.62, 30.79.
$C_8H_7ON_3$. Computed %: C 52.55; H 5.11; N 30.66.

2) Action of an alkali solution upon Substance (C). 1 g of the substance with a m.p. of 173° was boiled for an hour with a 40% solution of potassium hydroxide. After cooling the substance was extracted with ether. The ether solution was mixed with an alcoholic solution of picric acid. The resulting picrate fused at 216-217°. A test sample mixed with α-aminopyridyl picrate exhibited no depression.

3) Condensation of Substance (C) with aniline hydrochloride. A mixture of 0.6 g of the substance with a m.p. of 173° and 0.6 g of aniline hydrochloride was heated for 4 hours to 150-160° over an oil bath. After heating was over, the reaction mass crystallized. The mass was melted, the melt was dissolved in boiling alcohol, and the solution was filtered. When the filtrate was cooled, long fibrous crystals with a m.p. of 179-181° settled out. A test sample mixed with α-(phenyl)-N'-(pyridyl-2)-urea exhibited no depression.

We concluded, from these experiments, that Substance (C), with a m.p. of 173°, was N-(pyridyl-2)-urea.

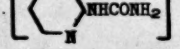
The structure of Substance (B), with a m.p. of 155-156.5°, was demonstrated as follows: 1) Analysis of Substance (B):

4.440 mg substance: 6.987 mg CO_2; 2.260 mg H_2O.
3.660 mg substance: 5.750 mg CO_2; 1.895 mg H_2O.
2.655 mg substance: 0.836 ml N_2 (25°, 747 mm).
3.145 mg substance: 0.980 ml N_2 (24°, 750 mm).
Found %: C 42.92, 42.85; H 5.70, 5.79; N 35.45, 35.36.
$C_7H_{11}O_2N_5$. Computed %: C 42.64; H 5.58; N 35.53.

2) Reaction of Substance (B) with water. 1 g of the substance with a m.p. of 155-156.5° was boiled with 10 ml of water or with a 1% solution of potassium hydroxide. When the solution was cooled, crystals with a m.p. of 173° settled out; they exhibited no depression in a test sample mixed with the N-(pyridyl-2)-urea we had synthesized. The mother liquor was evaporated and some drops of concentrated nitric acid was added to it. The precipitate that formed was drawn off by suction and desiccated. M.p. 149-150°. A test sample mixed with urea nitrate exhibited no depression.

3) Fusing N-(pyridyl-2)-urea with urea. A mixture of 1.4 g of N-(pyridyl-2) urea and 0.3 g of urea was heated over a 150° oil bath. The resulting substance was recrystallized from pyridine. M.p. 151°. A test sample mixed with Substance (B) (m.p. 155-156.5°) exhibited no depression.

These experiments established the fact that Substance (B), with a m.p. of 155-156.5°, is a molecular compound of N-(pyridyl-2)-urea with urea:



The methyl sulfomethylate of N-(pyridyl-2)-urea. 0.5 g of N-(pyridyl-2)-urea and 0.5 g of dimethyl sulfate were dissolved in 5 ml of benzene and boiled in a flask fitted with a reflux condenser over a water bath for 4 hours. The precipitate that settled out was filtered out, washed repeatedly on the filter with benzene, and crystallized from alcohol. M.p. 140-142°.

The substance consists of colorless lamellar crystals, which are readily soluble in cold water, poorly soluble in cold alcohol, and somewhat more soluble in hot alcohol.

6.060 mg substance: 0.834 ml N_2 (24°, 755 mm).
5.930 mg substance: 0.821 ml N_2 (24°, 755 mm).
Found %: N 15.72, 15.81.
$C_8H_{13}O_5N_3S$. Computed %: N 15.97.

The hydrochloride of N-(pyridyl-2)-urea. Colorless needles with a m.p. of 208-209°, which are highly soluble in water, slightly soluble in cold alcohol, and more soluble in hot alcohol.

4.264 mg substance: 0.894 ml N_2 (24°, 752 mm).
4.413 mg substance: 0.924 ml N_2 (23°, 754 mm).
Found %: N 23.84, 23.96.
$C_6H_8ON_3Cl$. Computed %: N 24.21.

Reaction of α-Aminopyridyl Hydrochloride with Potassium Cyanate (By. O. Fischer's Method)

A mixture of 3.2 g of the hydrochloride of α-aminopyridine, 2 g of potassium cyanate, and 5 ml of water was boiled over a screen for 10 hours. When boiling was over, a deposit (0.3 g) was formed, its heterogeneity being apparent to the naked eye. Triple crystallization from water yielded 0.15 g of a substance with

a m.p. of 175-176°. A test sample mixed with the N-(pyridyl-2) urea (m.p. 173°) or with N,N'-di-(pyridyl-2)-urea exhibited no depression of the melting point.

According to the analysis data, the substance has the composition of pyridylbiuret.

3.421 mg substance: 5.874 mg CO_2; 1.471 mg H_2O.
3.600 mg substance: 0.971 ml N_2 (23°, 750 mm).
3.250 mg substance: 0.870 ml N_2 (23°, 754 mm).
Found %: C 46.86; H 4.81; N 30.69, 30.62.
Dipyridylbiuret: $C_7H_8O_2N_4$. Computed %: C 46.67; H 4.44; N 31.11.
Monopyridylurea: $C_6H_7ON_3$. Computed %: C 52.55; H 5.11; N 30.66.
According to Fischer: Found %: N 30.8.

The Action of Phosgene on α-Aminopyridine

Experiment 1. 5 g of α-aminopyridine was dissolved in 50 ml of toluene, and 5.2 g of phosgene dissolved in 13.5 g of toluene was added to the solution with constant stirring. After all the phosgene had been added, the reaction mixture was heated to 50° for 2 hours. When the solution had cooled down, acicular crystals settled out; they were filtered out by suction, washed with toluene, and dissolved in water. The resulting toluene layer was separated, and the aqueous solution was alkalinized with a 25% solution of sodium hydroxide. This caused a yellow amorphous deposit to settle out, which was filtered out and desiccated. After crystallization from benzene, the substance consisted of colorless needles with a m.p. of 175°. The yield was 1.8 g (32% of the calculated quantity). A test sample mixed with N,N'-di(pyridyl-2)-urea exhibited no depression.

Experiment 2. Reaction of α-aminopyridine with phosgene in the presence of sodium amide. 7.5 g of α-aminopyridine was dissolved in 70 ml of anhydrous toluene, and 3 g of sodium amide, triturated under toluene, was added to the solution at room temperature, with constant stirring. After all the sodium amide had been added, the mixture was stirred for 3 hours at 35-40°. After stirring, a solution of 7.8 g of phosgene in 20 ml of toluene was added to the mixture. After all the phosgene had been added, the mixture was stirred until the evolution of heat had ceased. After the mixture had cooled, a red-brown deposit settled out, and the liquid was decolorized. The precipitate was filtered out by suction and added in small batches to 50 ml of water, almost all of it dissolving (except for a small quantity of tar). The toluene layer, in which the substance was steeped, floated on top. The aqueous layer was separated from the toluene and the tar, and then neutralized with a solution of sodium hydroxide until its reaction was weakly alkaline. The brown precipitate that settled out was recrystallized from benzene. This yielded 4.0 g of a substance with a m.p. of 173-175° (47% of the computed quantity). A test sample mixed with N,N'-di-(pyridyl-2)-urea exhibited no depression.

The Reaction of Ethyl Carbamate with α- Aminopyridine

A mixture of 2 g of ethyl carbamate and 2 g of an α-aminopyridine was heated to 180° over an oil bath for 5 hours. Bubbles of gas were evolved during the heating. After heating was complete, an oily substance was formed, which gradually crystallized when it was triturated with water. The precipitate was filtered out and repeatedly crystallized from alcohol; its m.p. was 174-176°. A test sample mixed with N,N'-di-(pyridyl-2)-urea exhibited no depression.

Condensation of β-Aminopyridine with Urea

A mixture of 4.2 g of β-aminopyridine and 5 g of urea was placed in a round bottomed flask and heated to 160° over an oil bath for 4 hours. Ammonia was evolved copiously during the reaction. After the reaction was over, the transparent liquid

was poured into twice its weight of alcohol. After the solution had cooled, slightly colored needles settled out. The precipitate was filtered out and crystallized from alcohol. The m.p. was 178-179°. Yield = 1.5 g.

The substance consists of pinkish lamellar crystals, which are readily soluble in alcohol and water.

3.915 mg substance: 3.539 mg CO_2; 1.834 mg H_2O.
4.095 mg substance: 7.799 mg CO_2; 1.900 mg H_2O.
Found %: C 52.55, 52.62; H 5.24, 5.25.
$C_6H_7ON_3$. Computed %: C 52.55; H 5.11.

The hydrochloride of N-(pyridyl-3)-urea. Colorless needles with a m.p. of 174-175° (from alcohol). In the determination of the melting point the substance was dropped into an apparatus heated to 160°. Sudden fusion took place at 174-175°. The contents of the capillary hardened when heating was continued still higher.

The substance is soluble in water, readily soluble in hot alcohol, and less so in cold alcohol.

2.970 mg substance: 0.627 ml N_2 (24°, 753 mm).
2.860 mg substance: 0.609 ml N_2 (23°, 755 mm).
Found %: N 24.04, 24.39.
$C_6H_8ON_3Cl$. Computed %: N 24.21.

Condensation of 2-Amino-5-nitropyridine With Phosgene

1 g of 2-amino-5-nitropyridine was dissolved in 50 ml of tetralin, and 0.3 g of sodium amide was added, with constant stirring, to the solution heated to 135°, after which the mixture was stirred for 2 hours. Then a solution of 0.7 g of phosgene in 1.7 g of toluene was added to the reaction mixture. This caused a precipitate to settle out, which was filtered out and added in small batches to water. Recrystallization from water yielded a substance with a m.p. of 187°, which exhibited no depression when mixed with 2-amino-5-nitropyridine.

Condensation of α-Aminopyridine (By the Schmid and Becker Method).

A mixture of 4 g of α-aminopyridine and 10 g of urea was heated to 180-185° for 3 hours over an oil bath. The melted mass was poured into water. The precipitate was filtered out by suction and desiccated.

0.5 g of the substance was boiled with 10 ml of benzene. The undissolved precipitate was filtered out by suction, desiccated, and weighed. The weight of the precipitate had not changed, which indicates that no N,N'-di-(pyridyl-2)-urea was present in the mixture. The substance is insoluble in alcohol. It crystallizes from water, but does not fuse.

N,N'-Di-(2-dimethylaminopyridyl-5)-urea

A mixture of 1.5 g of 2-dimethylamino-5-aminopyridine and 0.3 g of urea was heated for 4 hours over an oil bath.

The dark substance that resulted was washed repeatedly with ether and benzene. This yielded 0.9 g of a substance. Double crystallization from dilute alcohol (3 parts of water, 7 parts of alcohol) yielded a crystalline substance in the form of silvery lamellae. (In crystallization, 15 parts of alcohol were taken to 1 part of the substance by weight.) The air-dried substance fused at 252°.

3.622 mg substance: 0.851 ml N_2 (23°, 741 mm).
2.816 mg substance: 0.662 ml N_2 (19°, 749 mm).
Found %: N 26.42, 26.76.
$C_{15}H_{22}N_8O_2$. Computed %: N 26.41.

0.1134 g substance: loss in weight (during heating to 100° in vacuum) – 0.006 g.
Found %: loss in weight 5.29.
$C_{15}H_{20}ON_6H_2O$. Computed %: loss in weight 5.66.

SUMMARY

1. It has been found that heating α-aminopyridine with urea to 150° results in the formation of a molecular compound of pyridyl-2-urea with urea, which is transformed into pyridyl-2-urea when boiled in water.

2. It has been established that the statements of Schmid and Becker to the effect that the condensation of 2-aminopyridine with urea at 180° results in the formation of N,N'-di-(pyridyl-2)-urea are false.

3. It has been established that O. Fischer's assertion that the condensation of α-aminopyridine hydrochloride with potassium cyanate results in the formation of N-(pyridyl-2)-urea is erroneous.

4. It has been found that the condensation of α-aminopyridine with phosgene or with ethyl carbamate results in the formation of N,N'-di-(pyridyl-2)-urea.

5. It has been found that the condensation of 2-dimethylamino-5-aminopyridine with urea results in the formation of N,N'-di-(2-dimethylaminopyridyl-5)-urea.

6. It has been found that the condensation of 3-aminopyridine with urea results in the formation of N-pyridyl-3-urea.

LITERATURE CITED

[1] Schmid and Becker, Monatsh., 46, 671 (1925).

[2] O. Fischer, Ber., 32, 1297 (1899).

[3] Camps, Arch. Pharm. 274, 418-435 (1936).

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THE REACTION OF HETEROCYCLIC AMINES WITH UREA

II. THE REACTION OF SOME AMINO DERIVATIVES OF THIAZOLE AND QUINOLINE WITH UREA

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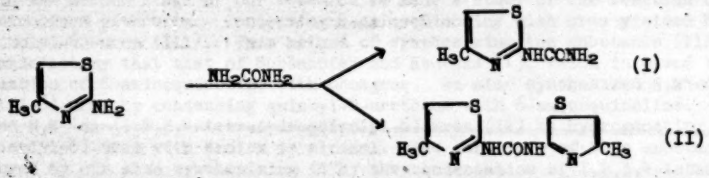
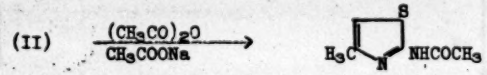
No research has been done as yet on condensations of the aminothiazoles with urea. We have made a study, principally, of the reaction of urea with 2-amino-4-methylthiazole.

Condensation was performed by fusing the above-mentioned substances at 130-140°. Two substances were recovered from the reaction mixture: 1) a substance with a m.p. of 236-238°, which is soluble in water; and 2) a substance with a m.p. of 270°, which is insoluble in water or in most organic solvents and crystallizes out of pyridine. Analysis has shown that the substance that is soluble in water is methylthiazoleurea, while the substance that is insoluble in water is di-(methylthiazolyl)-urea. Hence, the reaction proceeds as follows:



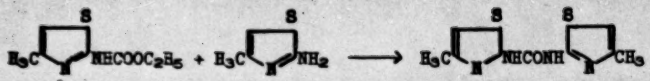
The two substances were separated by means of their differing solubility in water. We proved the structure of N,N'-di-(4-methylthiazolyl-2)-urea (II) by heating this substance with a mixture of acetic anhydride and sodium acetate, resulting in the formation of 2-acetoamino-4-methylthiazole.



The second procedure for proving the structure of N,N'-di-(4-methylthiazolyl-2)-urea was as follows.

(4-Methylthiazolyl-2)-urea:

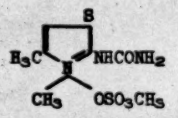
was synthesized for the first time by reacting the chlorocarbonate with 2-amino-4-methylthiazole. The reaction of this new compound with 2-amino-4-methylthiazole:



yielded a substance that was the same as (II).

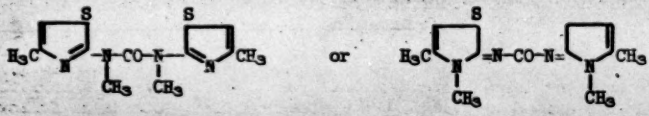
We proved the structure of Substance (I) by demonstrating that it was converted into (II) when heated above its melting point.

It is worthy of note that dimethyl sulfate reacts differently with N-(4-methylthiazolyl-2)-urea and N,N'-di-(4-methylthiazolyl-2)-urea. N-(4-methylthiazolyl-2)-urea reacts with dimethyl sulfate to form methyl sulfomethylate (Ia):

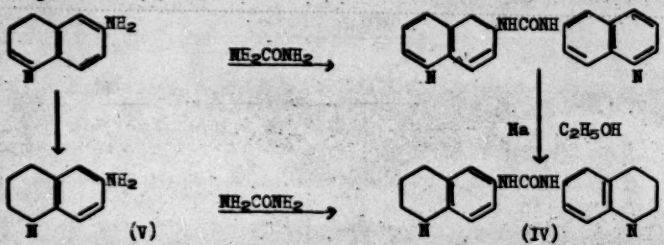


(Ia)

whereas heating N,N'-di-(4-methylthiazolyl-2)-urea with dimethyl sulfate yields a substance whose composition is that of the product of the substitution of two methyl groups for hydrogen atoms. This substance apparently has the following structure:



In the second stage of our research we made a study of the reaction of the aminoquinolines with urea. Condensing 6-aminoquinoline with urea yielded N,N'-di-(quinolyl-6)-urea (III). This method of synthesizing the substance (III) was more satisfactory that that of Schönhofer and Henecka [1], which involved the condensation of 6-aminoquinoline with phosgene. We also synthesized N,N'-di-(quinolyl-6)-urea by condensing quinoyl-6-urethane with 6-aminoquinoline. We produced N,N'-di-(1,2,3,4-tetrahydroquinolyl-6)-urea (IV) by hydrogenating N,N'-di-(quinolyl-6)-urea with sodium in alcohol. The structure of this substance was proved by our also synthesizing it by the condensation of 1,2,3,4-tetrahydro-6-aminoquinoline (V) with urea.



We synthesized 1,2,3,4-tetrahydro-6-aminoquinoline (V) by hydrogenating 6-aminoquinoline with sodium in alcohol. This method was more satisfactory than other procedures for synthesizing Substance (V).

EXPERIMENTAL

(In association with D. A. Livshits)

Condensing 2-amino-4-methylthiazole with urea. A mixture of 25 g of 2-amino-4-methylthiazole and 6.5 g of urea was placed in a porcelain crucible and heated over a low Bunsen burner for 2.5 hours while stirred with a glass rod. The temperature of the reaction mixture was kept at 130-140°. At the start of the reaction the mass looked like a rather mobile liquid, easily stirred with the rod, but toward the end it thickened so much that further stirring became impossible. The solidified melt was pulverized and boiled with 300 ml of water, in which only a small portion of the product dissolved. The hot solution was suction-filtered. A dark substance (A) remained on the filter. When the mother liquid cooled off, colorless crystals (B) settled out. The product (B) was extracted with water three times, after which it was crystallized from water (1 part of the substance to 30 parts of water).

2.862 mg substance: 0.650 ml N_2 (20°, 761.8 mm).
4.481 mg substance: 3.941 ml 0.02 N I_2, 1.178 ml 0.02 N $Na_2S_2O_3$.
4.134 mg substance: 3.941 ml 0.02 N I_2, 1.359 ml 0.02 N $Na_2S_2O_3$
Found %: N 26.53; S 19.77, 20.02.
$C_5H_7ON_3S$. Computed %: N 26.75; S 20.38.

N-(4-Methylthiazolyl-2)-urea is a colorless crystalline substance, hardly soluble in alcohol and insoluble in ether and benzene. It crystallizes from water as colorless rhombic crystals. The substance first fused at 195-197°, but solidifies again upon further heating and fuses again at 236-238°. The substance (A), which did not dissolve in water, was dried and recrystallized three times from pyridine. M.p. 270-270.5°.

5.200 mg substance: 1.019 ml N_2 (23°, 741.8 mm).
4.200 mg substance: 0.991 ml N_2 (23°, 741.8 mm).
Found %: N 22.04, 22.24.
$C_8H_{10}ON_4S_2$. Computed %: N 22.05.

N,N'-Di-(4-methylthiazolyl-2)-urea is not soluble in water or ether, and is poorly soluble in hot alcohol, pyridine, and quinoline. It crystallizes from pyridine as yellowish crystals.

N-(4-Methylthiazolyl-2)-urea hydrochloride. 2 g of N-(4-methylthiazolyl-2)-urea was dissolved in 6 ml of alcoholic hydrochloric acid, and 10 ml of alcohol and 20 ml of absolute ether were added to the solution. The substance consisted of acicular colorless crystals with a m.p. of 142-144° (from alcohol), containing one molecule of water of crystallization, as shown by analysis. The anhydrous salt fused at 176-177°.

2.850 mg substance: 0.488 ml N_2 (19°, 757 mm).
2.916 mg substance: 0.493 ml N_2 (19°, 759 mm).
2.913 mg substance: 3.941 ml 0.02 N I_2, 2.545 ml 0.02 N $Na_2S_2O_3$.
4.138 mg substance: 3.941 ml 0.02 N I_2, 1.935 ml 0.02 N $Na_2S_2O_3$.
Found %: N 19.97, 19.80; S 15.37, 15.53.
$C_5H_8ON_3SCl \cdot H_2O$. Computed %: N 19.86; S 15.13.
0.8146 g substance: loss at 100° 0.0716 g H_2O.
Found %: H_2O 8.79.
$C_5H_8ON_3SCl \cdot H_2O$. Computed %: H_2O 8.51.
Found: M 193.2.
$C_5H_8ON_3SCl$. Computed: M 193.5.

Methylsulfomethylate of N-(4-methylthiazolyl-2)-urea. A mixture of 2.8 g of N-(methylthiazolyl-2)-urea, 3.6 g of dimethyl sulfate, and 14 ml of anhydrous benzene was boiled for 3 hours over a water bath. The precipitate was suction-filtered,

washed with a small quantity of alcohol, and desiccated at 100°. The yield was 4.5 g; the m.p. 160-162°. Crystallization from alcohol yielded 2.9 g of a substance with a m.p. of 160-162°. The substance consisted of colorless cubic crystals, readily soluble in cold water and in hot alcohol.

3.852 mg substance: 0.488 ml N_2 (20°, 751 mm).
3.770 mg substance: 0.478 ml N_2 (22°, 751 mm).
Found %: N 14.49, 14.50.
$C_7H_{13}O_5N_3S_2$. Computed %: N 14.84.

Action of dimethyl sulfate on N,N'-di-(4-methylthiazolyl-2)-urea. A mixture of 4.6 g of N,N'-di-(4-methylthiazolyl-2)-urea, 6.1 g of dimethyl sulfate, and 24 g of benzene was boiled for three hours over a water bath. After the reaction was over, an oily substance covered the bottom of the flask. The benzene was decanted off, and the oily product was triturated in alcohol, which resulted in crystallization of the substance. This yielded 3.5 g of a substance with a m.p. of 177°, which was recrystallized from nitrobenzene. The substance fused at 228° after the first recrystallization, at 231° after the second, and at 231° after the third.

The substance is insoluble in water, poorly soluble in alcohol, and soluble in hot nitrobenzene.

3.910 mg substance: 0.705 ml N_2 (25°, 747 mm).
3.860 mg substance: 0.689 ml N_2 (25°, 745 mm).
Found %: N 20.25, 20.04.
$C_{11}H_{14}ON_4S_2$. Computed %: N 19.86.

Action of a mixture of acetic anhydride and sodium acetate upon N,N'-di-(4-methylthiazolyl-2)-urea. A mixture of 1 g of N,N'-di-(4-methylthiazolyl-2)-urea, 0.5 g of sodium acetate, and 4.8 g of the acetic anhydride was boiled over a screen for 4 hours. The precipitate was filtered out with suction. The filtrate was diluted with 40 ml of water and neutralized with soda. The precipitate that settled out of the solution was suction-filtered, washed with water, and recrystallized from alcohol. M.p. 130-133°. A test sample mixed with 2-acetylamino-4-methylthiazole exhibited no depression.

N-(4-Methylthiazolyl-2)-urethane. 1.2 g of chlorocarbonic ester was added drop by drop to a solution of 1.6 g of 2-amino-4-methylthiazole in 20 ml of absolute ether. As the ester was added, the solution turned cloudy, and crystals settled to the bottom of the flask together with an oily substance which soon crystallized. A 10% soda solution was added to the reaction mass. Two layers resulted: an aqueous-alkaline layer (A) and an ether layer, which contained colorless crystals (B) in suspension. The ether layer was separated, and the crystals were filtered out with suction. The ether was driven off. The substance secured after the ether had been driven off was combined with the crystals (B) and crystallized from alcohol. M.p. 99-100°.

N-(4-Methylthiazolyl-2)-urethane is a colorless substance that is insoluble in water and readily soluble in ether. It crystallizes from alcohol as colorless crystals.

4.190 mg substance: 0.551 ml N_2 (20°, 747 mm).
3.820 mg substance: 0.512 ml N_2 (24°, 747 mm).
Found %: N 15.05, 15.14.
$C_7H_{10}O_2N_2S$. Computed %: N 15.05.

The aqueous-alkaline layer (A) was extracted with ether. The oily substance left after the ether had been driven off was dissolved in alcohol and decanted from the alcoholic solution into picric acid. The resulting picrate fused at 222-223° after crystallization from alcohol. A test sample mixed with the picrate of 2-amino-4-methylthiazole exhibited no depression.

Condensing α-pyridylurethane with 2-amino-4-thiazole. A mixture of 2 g of α-pyridylurethane and 1.6 g of 2-amino-4-methylthiazole was heated to 150° for 3 hours over an oil bath. At first the mass fused, solidifying immediately thereafter. The solidified mass was triturated and repeatedly boiled with water. The substance (A) that was insoluble in water was filtered out with suction. When the filtrate cooled, the substance (B) settled out; it fused at 175-177° after double recrystallization from water.

4.017 mg substance: 0.860 ml N_2 (21°, 737 mm).
3.717 mg substance: 0.795 ml N_2 (21°, 741 mm).
Found %: N 24.11, 24.21.
$C_{10}H_{10}ON_4S$. Computed %: N 23.93.

Analysis indicated that the substance (B) has the composition of N-(4-methylthiazolyl-2)-N'-(pyridyl-2)-urea.

The substance (B) that was insoluble in water was recrystallized from pyridine; m.p. 264-266°. A test sample mixed with N,N'-di-(4-methylthiazole-2)-urea exhibited no depression.

Condensing (4-methylthiazolyl-2)-urethane with 2-amino-4-methylthiazole. A mixture of 0.5 g of (4-methylthiazolyl-2-urethane and 0.3 g of 2-amino-4-methylthiazole was heated over a screen. The product melted, and alcohol was evolved. The mixture solidified after a time. The yield was 0.7 g. Crystallization from pyridine yielded a substance with a m.p. of 267-268°. A test sample exhibited no depression when mixed with N,N'-di-(4-methylthiazolyl-2)-urea. Yield 0.3 g.

Hydrogenation of 6-aminoquinoline. 6 g of 6-aminoquinoline was dissolved in 120 ml of amyl alcohol, and the solution was placed in a flask, fitted with a reflux condenser, a stirrer, and a side outlet. The flask was heated to 130-150° over an oil bath, and 12 g of metallic sodium was added to the solution at this temperature with constant stirring. After all the sodium had been added, the mixture was decomposed with water. The amyl-alcohol layer was extracted with hydrochloric acid. Alkalinization resulted in the recovery of an oily substance, which was extracted with ether. The ether was driven off, and the residue was distilled. B.p. 130-135° at 1 mm; m.p. 95-97° (Ziegler gives the m.p. as 97°).

When the substance is reacted with ferric chloride in dilute acetic acid, the solution turns red, changing to green after dilute hydrochloric acid is added.

Condensing 6-amino-1,2,3,4-tetrahydroquinoline with urea. A mixture of 1 g of 6 amino-1,2,3,4-tetrahydroquinoline and 0.2 g of urea was heated to 120-130° for 4 hours. 15 minutes after heating was begun, ammonia was evolved at 125°, which was proved by the evolution of bubbles of gas, by its odor, and by its turning litmus paper blue. After the dark melt had cooled, it was pulverized and boiled with alcohol. This yielded 0.5 g of a substance with a m.p. of 237-240°. The substance turns red when reacted with ferric chloride in dilute acetic acid, changing to green when dilute hydrochloric acid is added. Crystallization from pyridine yields colorless crystals in the shape of lamellar needles. M.p. 239-240.5°. The substance is insoluble in hot alcohol, benzene, and water.

2.685 mg substance: 0.409 ml N_2 (20°, 744 mm).
2.379 mg substance: 0.368 ml N_2 (20°, 744 mm).
Found %: N 17.37, 17.64.
$C_{18}H_{22}ON_4$. Computed %: N 17.39.
4.195 mg substance: 10.945 mg CO_2; 2.595 mg H_2O.
3.602 mg substance: 9.423 mg CO_2; 2.260 mg H_2O.
Found %: C 71.20, 71.39; H 6.92, 7.02.
$C_{18}H_{22}ON_4$. Computed %: C 70.81; H 6.83.

N,N'-Di-(1,2,3,4-tetrahydroquinolyl-6)-urea hydrochloride. 0.5 g of N,N'-di-(1,2,3,4-tetrahydroquinolyl-6)-urea was treated with alcoholic hydrochloric acid and ether. This yielded a substance of m.p. 254°.

3.648 mg substance: 2.615 mg AgCl.
5.422 mg substance: 3.875 mg AgCl.
Found %: Cl 17.73, 17.67.
$C_{19}H_{24}ON_4Cl_2$. Computed %: Cl 17.97.

Synthesis of N,N'-diquinolyl-6 urea. 1. Condensation of 6-aminoquinoline with urea. A mixture of 8 g of 6-aminoquinoline and 1.76 g of urea was heated to 130-160° for 10 hours over an oil bath. Ammonia was liberated during the reaction. The mixture solidified after heating was over. The melt was pulverized and dissolved in dilute hydrochloric acid. The base was precipitated with aqueous ammonia, desiccated, and crystallized from aqueous alcohol. M.p. 272-273°. The m.p. was 273-274° after repeated crystallization from alcohol and from nitrobenzene (Schönhöfer and Henecka give the m.p. as 260-262°).

2. Condensing (quinolyl-6)-urethane with 6-aminoquinoline. 1 g of 6-aminoquinoline was triturated with 1.5 g of (quinolyl-6)-urethane. The mixture was placed in a Würtz flask and heated for 1.5 hours over a metallic bath at a temperature of 160-170° (the temperature of the reaction mixture being 140-150°). The alcohol driven off during the reaction was collected in a receiver. This yielded 0.2 g of alcohol. The substance remaining in the Würtz flask fused at 196-200°. The substance fused at 266-268° after crystallization from aqueous alcohol. Yield 1.2 g.

Hydrogenation of N,N'-di-(quinolyl-6)-urea. A solution of 3 g of N,N'-di-(quinolyl-6)-urea in 120 ml of absolute ethyl alcohol was placed in a flask fitted with a reflux condenser, a stirrer and a stoppered outlet. The flask was placed over an oil bath and heated to 90-100°. At this temperature, 7 g of metallic sodium was added in small batches with constant stirring; hydrogen was liberated, and the liquid boiled. After all the sodium had been added, water was added to the mixture. The resulting precipitate was filtered out with suction, washed with water, and desiccated. The substance is insoluble in water, nearly insoluble in alcohol, and soluble in hot nitrobenzene and pyridine. M.p. 200°. M.p. 216-218° after crystallization from nitrobenzene; the substance fused at 234-239° after subsequent recrystallization from pyridine. A test sample exhibited no depression when mixed with the condensation product of 6-amino-1,2,3,4-tetrahydroquinoline and urea (m.p. 239.0-240.5°). The substance turns red when reacted with ferric chloride in acetic acid, changing to green with dilute hydrochloric acid.

The identity of Substance (A), synthesized by hydrogenating N,N'-di-(quinolyl-6)-urea, and Substance (B), produced by condensing urea with 6-amino-1,2,3,4-tetrahydroquinoline, is evident from a comparison of their properties:

	Substance (A)	Substance (B)
Melting point	234-239°	239-240.5°
Mixed sample, m.p.	236-239°	
Color with ferric chloride in acetic acid.....	Red, changing to green when hydrochloric acid is added	The same
Kind of crystals.....	Lamellar needles	Lamellar needles
Solubility in alcohol.....	Poor	Poor
Solubility in pyridine.....	Poor	Poor

SUMMARY

1. It has been found that condensing 2-amino-4-methylthiazole with urea yields N-(4-methylthiazolyl-2)-urea and N,N'-di-(4-methylthiazolyl-2)-urea.

2. It has been shown that condensing 6-aminoquinoline with urea, as well as with (quinolyl-6)-urethane, yields N,N'-di-(quinolyl-6)-urea.

3. It has been found that hydrogenating N,N'-di-(quinolyl-6)-urea or condensing 1,2,3,4-tetrahydro-6-aminoquinoline with urea yields N,N'-di-(1,2,3,4-tetrahydroquinolyl-6)-urea.

LITERATURE CITED

[1] Schönhofer and Henecka. German patent 583207.

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EXCHANGE REACTIONS OF UREA DERIVATIVES

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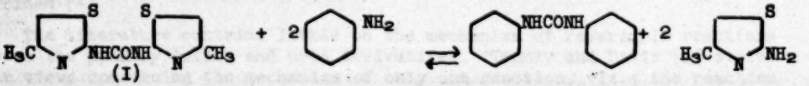
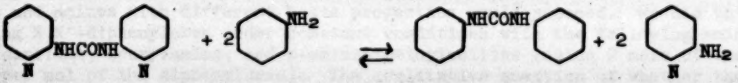
In our study of the heterocyclic derivatives of urea, we synthesized N,N'-di-(4-methylthiazolyl-2)-urea (I) among other substances. The base recovered from the reaction was difficultly soluble in the usual inert solvents. On the strength of this we tried to recrystallize it from aniline, in which it was readily soluble. The substance dissolved in aniline after brief heating. After the solution cooled, acicular crystals, which were N,N'-diphenylurea, with a m.p. of 236° settled out of the mother liquor. This led us to the following conclusion: when N N'-di-(4-methylthiazolyl-2)urea is heated with aniline, it is transformed into N,N'-diphenylurea as follows:



(I)

We were also interested in making a study of the applicability of this kind of substitution reaction to other derivatives of urea. With this in view, we reacted aniline with various heterocyclic derivatives of urea, in all cases recovering N,N'-diphenylurea and heterocyclic amines. Thus, heating N,N'-di-(pyridyl-2)-urea with an excess of aniline yields N,N'-diphenylurea and 2-aminopyridine:



Heating N,N'-di-(quinolyl-6)-urea with an excess of aniline gives rise to N,N'-diphenylurea and 6-aminoquinoline. In the same way, diphenylurea and 2-methoxy-6-chloro-9-aminoacridine are produced by heating N,N'-di-(2-methoxy-6-chloroacridyl-9)-urea with aniline. The exchange reactions of urea derivatives are reversible. In our subsequent study of these exchange reactions, we employed primary amines and substituted ureas, reacting them together in the following pairs:

p-Aminodipropylaniline + N,N'-diphenylurea
p-Aminodipropylaniline + N,N'-di-(4-methylthiazolyl-2)-urea
Benzylamine + N,N'-di-(4-methylthiazolyl-2)-urea
Benzylamine + N,N'-diphenylurea
2-Amino-4-methylthiazole + N,N'-diphenylurea
α-Aminopyridine + N,N'-diphenylurea

With the exception of the last reaction, all these substitution reactions

resulted in the formation of symmetrical urea derivatives, as follows:

$$RNHCONHR + 2R'NH_2 \rightleftharpoons R'NHCONHR' + 2RNH_2$$

the reaction between 2-aminopyridine and N,N'-diphenylurea proceeding as follows:

$$RNHCONHR + R'NH_2 \rightleftharpoons R'NHCONHR + RNH_2.$$

The reactions between p-nitroaniline and N,N'-diphenylurea, between 6-aminoquinoline and diphenylurea, and between aniline and N,N'-di-(4-dipropylaminophenyl)-urea, however, did not take place under the conditions we ordinarily employed for the substitution reactions. Later on, in our study of the mechanism of the exchange reactions of urea derivatives, we discovered the explanation for this fact.

We carried out all the exchange reactions either without any solvent or in a solution of phenol, tetralin, or turpentine. The minimum temperature at which the reaction sets in is 130-140°.

Our searches have not turned up any papers in the literature that are specially devoted to the exchange reactions of urea derivatives. In indivdual papers merely a few instances are cited of reactions of this type, described by the authors in papers dealing with altogether different topics. Hofmann [1], for example, compared the properties of acetamide and urea derivatives, and found that boiling aniline with N-methyl-N'-acetylurea yields ammonia, methylamine, acetanilide, and diphenylurea. Michler [2] produced N,N'-di-(p-tolyl)-urea by heating N,N-diphenyl-N'-p-tolylurea with p-toluidine. Exchange reactions of the aryl phthalamic acids have also been described. B.A. Porai-Koshits [3], for instance, secured N-phenylphthalamic acid and methylaniline by reacting aniline with N-phenyl-N-methylphthalamic acid. Other instances of this sort have also been described [4].

The literature contains little on the mechanism of reversible reactions between the primary amines and urea derivatives. Tenney and Davis [5] state their views concerning the mechanism of only one reaction, viz.; the reaction between N,N'-diethylurea and aniline:

$$C_2H_5NHCONHC_2H_5 + 2C_6H_5NH_2 \rightleftharpoons C_6H_5NHCONHC_6H_5 + 2\ C_2H_5NH_2.$$

To explore the mechanism of reversible reactions of the urea derivatives experimentally, we ran tests that had as their objective settling the quantitative aspects of the problem and determining how the reactions between urea derivatives and amines with different basic properties would proceed. We did this by reacting N,N'-diphenylurea under constant conditions with the following amines: p-nitroaniline, benzylamine, and p-aminodimethylaniline (using 2 mols of the amine per mol of the diphenylurea). The qualitative question of whether the exchange reaction takes place was resolved by the formation of aniline. The reaction yield was measured by the quantity of the newly formed urea derivative (III).

The results of our tests showed that the more pronounced the basic properties of the amine (I), the higher the yield of the substituted urea (III).

$$\underset{\text{(II)}}{RNHCONHR} + \underset{\text{(I)}}{2R'NH_2} \rightleftharpoons \underset{\text{(III)}}{R'NHCONHR'} + 2RNH_2.$$

We may conclude from our data that when primary amines are reacted with a substituted urea, the equilibrium is displaced toward the formation of the amine whose basic properties are less pronounced.

When we compare this conclusion with the fact that aryl isocyanates combine readily with amines possessing strongly pronounced basic properties, as has been shown by Michael and Cobb [6], the reason for this sort of equilibrium shift is

TABLE 1

Test No.	Name of amine (I)	Dissociation constant of the amine	Reaction yield, %
1	p-Nitroaniline	$1 \cdot 10^{-12}$	0
2	6-Aminoquinoline	–	0
3	2-Aminoquinoline	$1.4 \cdot 10^{-7}$	16.3
4	p-Aminodipropylaniline	–	43.9
5	p-Aminodimethylaniline	$5.0 \cdot 10^{-7}$	77.2
6	Benzylamine	$2.4 \cdot 10^{-5}$	100

obvious, and we find a clearer basis for the mechanism of the reactions of primary amines with urea derivatives via the preliminary formation of aryl-(alkyl) isocyanates.

At bottom, when a primary amine (A) is heated together with a symmetrically substituted urea (B), the latter breaks down into an isocyanate (C) and a primary amine (D):

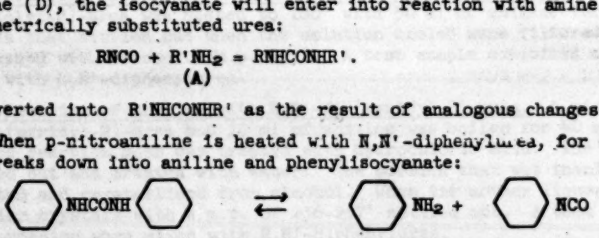
$$\underset{(B)}{RNHCONHR} \rightleftarrows \underset{(C)}{RNCO} + \underset{(D)}{RNH_2}.$$

When the basic properties of the amine (D) are greater than those of the amine (A), the isocyanate will enter into reaction only with the amine (D), giving rise to the initial urea derivative, (B). (In other words, the exchange reaction does not take place.) Conversely, i.e., when the amine (A) is more basic than the amine (D), the isocyanate will enter into reaction with amine (A), yielding an unsymmetrically substituted urea:

$$RNCO + \underset{(A)}{R'NH_2} = RNHCONHR'.$$

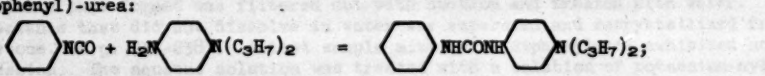
which is converted into R'NHCONHR' as the result of analogous changes.

When p-nitroaniline is heated with N,N'-diphenylurea, for example, the latter breaks down into aniline and phenylisocyanate:

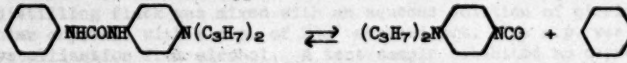


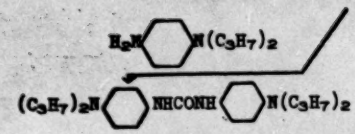
In view of the fact that p-nitroaniline is less basic than aniline, it will not react with the phenyl isocyanate. As a matter of fact, our experiments have shown that the reaction of p-nitroaniline with N,N'-diphenylurea does not result in the formation of N,N'-di-(4-nitrophenyl)-urea under ordinary conditions.

When p-aminodipropylaniline is heated with N,N'-diphenylurea, the reaction proceeds as follows: the phenyl isocyanate formed as the result of the decomposition of the diphenylurea will react with the p-aminodipropylaniline (because this amine is more strongly basic than aniline), yielding N-phenyl-N'-(dipropylaminophenyl)-urea:

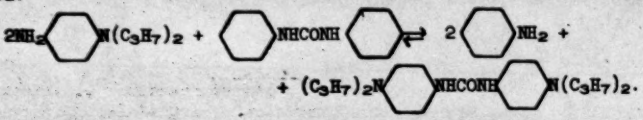


which in turn yields N,N'-di-(4-dipropylaminophenyl)-urea as the result of further transformations of the same type:





In fact, our experiments have shown that the reaction of p-aminodipropylaniline with N,N'-diphenylurea results in a high yield of N,N'-di-(4-dipropylaminophenyl)-urea:



EXPERIMENTAL

Experiments on the Reaction of Substituted Ureas with an Excess of Primary Amines

1. Reaction of aniline with N,N'-di-(4-methylthiazolyl-2)-urea. 0.5 g of N,N'-di-(4-methylthiazolyl-2)-urea was heated with 10 ml of aniline to 180° for 30 minutes. After the solution had cooled, colorless acicular crystals, with a m.p. of 235-236°, settled out. A test sample exhibited no depression when mixed with N,N'-diphenylurea.

2. Reaction of aniline with N-(4-methylthiazolyl-2)-urea. 1 g of N-(4-methylthiazolyl-2)-urea was heated to 180° with 30 ml of aniline for 20 minutes. The crystals that settled out when the solution cooled were filtered out with suction and washed with alcohol. M.p. 235°. A test sample exhibited no depression when mixed with N,N'-diphenylurea.

3. Reaction of aniline with N,N'-di-(pyridyl-2)-urea. A mixture of 0.3 g of N,N'-di-(pyridyl-2)-urea and 10 ml of aniline was boiled for 40 minutes. After heating, the reaction mass was treated with hydrochloric acid. The precipitate was filtered out and treated with water. The portion that was insoluble in water was separated and crystallized from alcohol. When the mother liquor cooled, colorless acicular crystals with a m.p. of 236-237° settled out. A test sample exhibited no depression when mixed with N,N'-diphenylurea.

The aqueous solution was treated with an alkali solution and extracted with ether. An ether solution of picric acid was added to the ether extract. This resulted in the precipitation of a picrate with a m.p. of 217°, which exhibited no depression when mixed with the picrate of α-aminopyridine.

4. Reaction of aniline with N,N'-di-(quinolyl-6)-urea. 0.8 g of N,N'-di-(quinolyl-6)-urea was heated to 180° with 20 g of aniline for 1 hour. After it had cooled, the reaction mass was acidulated with hydrochloric acid. The precipitate that formed was filtered out with suction and treated with water. The substance that did not dissolve in water was separated and recrystallized from acetone. M.p. 237-238°. A test sample mixed with diphenylurea exhibited no depression. The aqueous solution was treated with a solution of potassium hydroxide and extracted with ether. The ether was driven off, and the residue was treated with steam until all the aniline had been driven off. The solution remaining in the distilling flask was mixed with an aqueous solution of picric acid. Yellow acicular crystals with a m.p. of 236° settled out. The m.p. was 237-238° after recrystallization from alcohol. A test sample exhibited no depression when mixed with the picrate of 6-aminoquinoline.

5. Reaction of aniline with N,N'-di-(2-methoxy-6-chloroacridyl-9)-urea. 0.5 g

of N,N'-di-(2-methoxy-6-chloroacridyl-9)-urea was boiled with 5 ml of aniline. The base dissolved within a short time. Further heating caused a solid substance to rise to the surface of the liquid. After 3 hours of heating, the mixture was cooled and dilute hydrochloric acid was added. The precipitate that did not dissolve in the acid was filtered out by suction, washed with water, and dried. The dried substance was boiled with acetone. The precipitate that did not dissolve in acetone was separated and washed with an alkali solution. M.p. 274°. A test sample exhibited no depression when mixed with 2-methoxy-6-chloro-9-aminoacridine.

Acicular crystals with a m.p. of 230-235° settled out of the acetone. A test sample exhibited no depression when mixed with diphenylurea.

6. Reaction of 2-amino-4-methylthiazole with N,N'-diphenylurea. A mixture of 1 g of N,N'-diphenylurea and 5 g of 2-amino-4-methylthiazole was heated to 160° for 2 hours. The mass was treated with ether when it had cooled. The residue that did not dissolve in the ether was filtered out with suction, washed with ether, and recrystallized from pyridine. M.p. 264-265°. A test sample exhibited no depression with the N,N'-di-(4-methylthiazolyl-2)-urea secured by us by condensing 2-amino-4-methyl-thiazole with urea.

Reaction of N,N'-Diphenylurea with Equimolar Quantities of Various Amines

1. Reaction with Benzylamine. A solution of 2.1 g (0.01 mol) of diphenylurea and 2.1 g (0.02 mol) of benzylamine in 8 ml of tetralin was heated to 180° for 4 hours. The tetralin was driven off with steam together with aniline. An oily substance that soon crystallized was left behind in the flask. This yielded 2.4 g of a substance (100% of the computed quantity). The substance fused at 162-165° after crystallization from alcohol. A test sample exhibited no depression when mixed with N,N'-dibenzylurea.

2. Reaction with p-aminodimethylaniline. A solution of 4.2 g (0.02 mol) of diphenylurea and 5.4 g (0.04 mol) of p-aminodimethylaniline in 20 ml of turpentine was heated to 180° for 4 hours. After heating was over, the aniline and the turpentine were driven off with steam. The precipitate that remained in the flask was treated with hydrochloric acid. The acid solution was filtered and then treated with an alkali solution. The precipitate that was thrown down was filtered out with suction and washed with hot water. This yielded 4.6 g of a substance (77.18% of the theoretical). Its m.p. was 236-241° after crystallization from nitrobenzene. A test sample exhibited no depression when mixed with N,N'-di-(4-dimethylaminophenyl)-urea.

3. Reaction with p-aminodipropylaniline. 5.3 g (0.025 mol) of diphenylurea, 9.6 g (0.05 mol) of freshly distilled p-aminodipropylaniline, and 15 g of anhydrous phenol were placed in a round-bottomed flask fitted with a reflux condenser and heated to 180° over an oil bath for 4 hours. The reaction product, which was a dark oily substance with a bluish tinge, was dissolved in alcohol. Yellow acicular crystals settled out; they were filtered out and washed with alcohol. The yield was 4.5 g (43.9% c the computed quantity). A test sample exhibited no depression when mixed with N,N'-di-(4-dipropylaminophenyl)-urea.

The alcoholic filtrates were treated with an alkali solution (6.7 g of NaOH in 70 ml of water), and the whole was distilled with steam. This drove off the alcohol and the aniline. The residue in the distilling flask was an oily substance, part of which crystallized after benzene had been added and it was rubbed with a rod. The crystallized portion was separated. M.p. 238°. A test sample exhibited no depression when mixed with diphenylurea. The oily portion was apparently the product of the reaction of p-aminodipropylaniline with phenol.

4. Reaction with α-aminopyridine. A mixture of 10.6 g (0.05 mol) of N,N'-

diphenylurea, 9.4 g (0.1 mol) of α-aminopyridine, and 30 g of anhydrous phenol was heated to 180° (bath temperature) for 4 hours over an oil bath. After this heating, the reaction mass was treated with 150 ml of a 10% solution of potassium hydroxide. The precipitate that was thrown down was separated from the mother liquor and treated with steam. After all the aniline had been driven off, the precipitate was filtered out with suction and treated with dilute HCl (1:1). This caused part of the precipitate to dissolve. The undisolved part was filtered out, dried, and recrystallized from alcohol. M.p. 235-236°. No depression when mixed with diphenylurea.

The acid filtrate was precipitated with a 40% solution of potassium hydroxide. The precipitate was filtered out and recrystallized from alcohol. Elongated acicular crystals, with a m.p. of 186-187° settled out. A test sample exhibited no depression when mixed with N-(phenyl)-N'-(pyridyl-2)-urea. The yield was 1.1 g, 16.3% of the computed amount.

5. Reaction with 6-aminoquinoline. A mixture of 5.3 g of N,N'-diphenylurea, 7.2 g of 6-aminoquinoline, and 15 g of phenol was placed in a round-bottomed flask fitted with a reflux condenser and heated to 180° over an oil bath for four hours. After this heating the reaction mass consisted of an oily substance mixed with a crystalline deposit. The reaction mass was treated with a solution of caustic soda (6.7 g NaOH in 30 ml of water) and distilled with steam. We detected no aniline in the distillate, neither by its outward appearance nor by its reaction with pitric acid. The oily substance crystallized during the distillation with steam. The precipitate was filtered out with suction and, after having been washed with water, treated with 1:1 hydrochloric acid. Part of the substance dissolved. The precipitate (A) was filtered out and washed several times with hot water. The acid solution was evaporated to small volume in a beaker over a water bath. When the solution cooled crystals of 6-aminoquinoline hydrochloride settled out. Treatment of the salt with an alkali solution yielded 4.6 g of a substance with a m.p. of 113°, which exhibited no depression when mixed in a test sample with 6-aminoquinoline.

After the precipitate (A) had been treated with hydrochloric acid, it was recrystallized from alcohol. M.p. 229-230°. Weight 4.2 g. A test sample exhibited no depression when mixed with diphenylurea.

No other products besides the 6-aminoquinoline and the diphenylurea were recovered from the reaction mass.

6. Reaction of p-nitroaniline with N,N'-diphenylurea. 5.3 g of N,N'-diphenylurea, mixed with 6.8 g of p-nitroaniline and 15 g of phenol, was placed in a round-bottomed flask fitted with a reflux condenser and heated to 180° for 4 hours. The reaction mass, an oily liquid, was treated with a solution of caustic soda (6.7 g of NaOH in 70 ml of water). An oily substance separated out, which gradually crystallized. The aqueous layer and the precipitate were treated separately with steam. No aniline was found to have been driven off in either case. The solid residue in the distilling flask was a porous yellow mass that was insoluble in boiling hydrochloric acid or in carbon tetrachloride, but dissolved readily in hot alcohol, benzene, and ether. The substance was thoroughly extracted with ether. The ether extract was desiccated above $CaCl_2$, and the ether was driven off. The residue, a brown amorphous mass, was fractionally crystallized from aqueous pyridine. This yielded the following substances: a) a substance with a m.p. of 198° (light-yellow platelets); b) a substance with a m.p. of 204° (brown lamellae); and c) a substance that did not fuse up to 270° (a yellow amorphous substance).

The residue, which did not dissolve in ether (5.8 g), was a yellow-green mass that fused at 187-189°. None of the substances we secured corresponded to N,N'-di-(4-nitrophenyl)-urea in their properties or in their analysis.

SUMMARY

1. Exchange reactions were carried out between the following pairs of substances: aniline + N,N'-di-(4-methylthiazolyl-2)-urea; aniline + N,N'-di-(pyridyl-2)-urea; p-aminodipropylaniline + N,N'-diphenylurea; p-aminodimethylaniline + N,N'-diphenylurea; p-aminodipropylaniline + N,N'-di-(4-methylthiazolyl-2)-urea; benzylamine + N,N'-diphenylurea; and 2-amino-4-methylthiazole + N,N'-diphenylurea.

It was found that all these reactions follow the same pattern:

$$RNHCONHR + 2R'NH_2 \rightleftharpoons R'NHCONHR' + 2RNH_2.$$

2. It has been established that the reation of α-aminopyridine with N,N'-diphenylurea results in the formation of N-phenyl-N'-pyridylurea and aniline.

3. It has been found that neither the reaction between p-nitroaniline and N,N'-diphenylurea nor the reaction between 6-aminoaniline and N,N'-diphenyl urea takes place under the conditions under which the reactions specified under Point 1 above occur.

4. It has been established that the more pronounced the basic properties of the amine entering into an exchange reaction with substituted ureas, the higher the yields of the newly formed substituted urea.

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A DIENE SYNTHESIS WITH HEXADIENE-2,4

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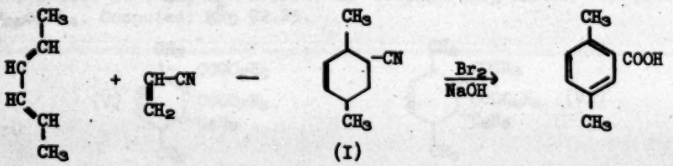
In our preceding report [1] we set forth data on the diene synthesis of piperylene with acrylic nitrile, and with ethylidene and benzylidene malonates and acetoacetates. We also ran parallel tests on the addition of these dienophilic compounds to hexadiene-2,4.

The results of these tests are reported in the present paper. Hexadiene is a less active diene than piperylene, and the yields of addition products in experiments using it were not high. Heating hexadiene with acrylic nitrile to 120-130° resulted in a yield of 40% (in terms of the acrylic nitrile) of the nitrile of 2,5-dimethyl-Δ^3-cyclohexenecarboxylic-1 acid (I), as a liquid with an almond odor and the following constants:

B.p. 82-83° at 8 mm; n_D^{20} 1.4678; d_4^{20} 0.9292; MR_D 40.83.
$C_9H_{13}NF$. Computed: MR_D 40.91.

Dehydrogenating the nitrile with bromine, as specified by Einhorn and Wilstätter [2], and then exposing it to the action of alkali yielded 2,5-dimethylbenzoic acid with a m.p. of 132° [3]:



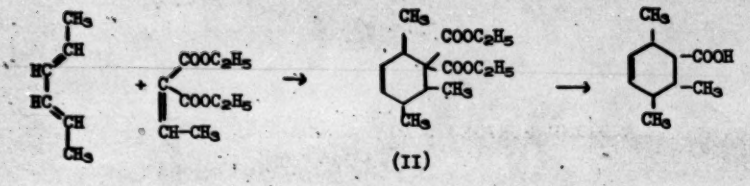
(I)

When hexadiene was reacted with ethylidene malonate and the constituents were heated to 170-175°, we got the diethyl ester of 2,5,6-trimethyl-Δ^3-cyclohexenedicarboxylic-1,1 acid (II), with a yield of 31% in terms of the ethylidene malonate.

The ester's constants were:

B.p. 128-129° at 5 mm and 144-145° at 10 mm; n_D^{20} 1.4641; d_4^{20} 1.0362, MR_D 71.48; $C_{15}H_{24}O_4F$. Computed: MR_D 72.11.

Saponifying the ester and heating until no more CO_2 was evolved yielded 2,5,6-trimethyl-Δ^3-cyclohexenecarboxylic-1-acid with a m.p. of 160-168° at 4 mm. The amide of the acid had a m.p. of 183-184°.



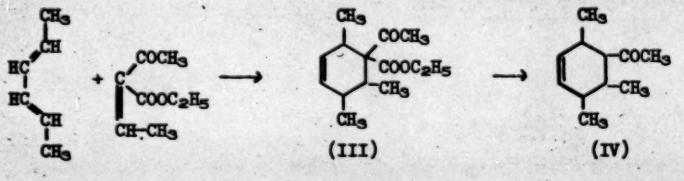
(II)

Heating hexadiene with ethylidene malonate to 180° resulted in the formation of the ethyl ester of 2,5,6-trimethyl-1-acetyl-Δ^3-cyclohexenecarboxylic-1 acid (III), with a yield of 40% in terms of the ethyl ester:

B.p. 115-117° at 4 mm; n_D^{20} 1.4744; d_4^{20} 1.0247. MR_D 65.59.
$C_{14}H_{22}O_3F$. Computed: MR_D 65.85.

Saponifying it with alcoholic caustic potash enabled us to recover the product of the ketonic cleavage, 2,5,6-trimethyl-1-acetyl-Δ^3-cyclohexene (IV).

The ketone had a b.p. of 115-118° at 22 mm; n_D^{20} 1.4651, and formed a semicarbazone with a m.p. of 165-167°:



(III) (IV)

Benzalmalonate is added to hexadiene at 180°, yielding the diethyl ester of 2,5-dimethyl-6-phenyl-Δ^3-cyclohexenedicarboxylic-1,1 acid (V) with a yield of 30%.

The ester is a thick liquid with the following constants:

B.p. 176-180° at 4 mm; n_D^{20} 1.5231; d_4^{20} 1.0945. MR_D 91.62.
$C_{20}H_{26}O_4F_4$. Computed: MR_D 92.23.

Under the same conditions, the reaction of benzal acetoacetate with hexadiene produced a yield of 40% of the ethyl ester of 2,5-dimethyl-6-phenyl-1-acetyl-Δ^3-cyclohexenecarboxylic-1 acid (VI), of which were as follows:

B.p. 163-165° at 3mm; n_D^{20} 1.5309; d_4^{20} 1.0866. MR_D 85.52.
$C_{18}H_{24}O_3F_4$. Computed: MR_D 85.34.

EXPERIMENTAL

The hexadiene used in the diene-synthesis reactions [4] had a b.p. of 78-83°; n_D^{20} 1.4495; d_4^{20} 0.7376.

1. Condensing Hexadiene-2,4 With Acrylic Nitrile.

30 g of hexadiene, 18 g of acrylic nitrile, and 0.1 g of hydroquinone were heated in sealed tubes to 120-130° for 12 hours. After the unreacted hexadiene and acrylic nitrile had been driven off, we secured 18 g (40%, based on the acrylic

nitrile) of 2,5-dimethyl-Δ^3-cyclohexenecarboxylic acid:

B.p. 82-83° at 8 mm; n_D^{20} 1.4678; d_4^{20} 0.9202; MR_D 40.83.
$C_9H_{13}N$ F. Computed: MR_D 40.91.

An oily liquid with the odor of almonds.

0.1105 g substance: 0.3233 g CO_2; 0.0955 g H_2O.
Found %: C 79.79; H 9.67.
$C_9H_{13}N$. Computed %: C 79.95; H 9.69.

Dehydrogenating and saponifying the nitrile. Accurately computed quantities of the nitrile (1.1 g) and of bromine (2.5 g) were heated to 200° for 2 hours in a sealed tube. The contents of the tube were boiled with 5 g of caustic soda, 5 ml of water, and 5 ml of alcohol for 18 hours. After the alcohol had been driven off, the solution was diluted with water and boiled with activated charcoal, after which it was acidulated with hydrochloric acid (1:1). The white precipitate that was thrown down was dried; after sublimation it yielded crystals with a m.p. of 132°, which agrees with the figures given in the literature [3] for 2,5-dimethylbenzoic acid.

2. Condensing Hexadiene with Ethylidene Malonate

25 g of ethylidene malonate, 17 g of hexadiene, and 0.2 g of hydroquinone were heated to 170-175° for 13 hours in sealed tubes. The unreacted original substances, the dimer, and the tar were separated by means of repeated vacuum distillation. This yielded 11.2 g (31%, based on the ethylidene malonate) of the diethyl ester of 2,5,6-trimethyl-Δ^3-cyclohexene-1,1-dicarboxylic acid:

B.p. 128-129° at 5 mm and 144-145° at 10 mm; n_D^{20} 1.4641; d_4^{20} 1.0362.
MR_D 71.48. $C_{15}H_{24}O_4$ F. Computed: MR_D 72.11.

A colorless, viscous liquid with a slight turpentine odor.

0.3590 g substance: 0.8801 g CO_2; 0.2877 g H_2O.
Found %: C 66.86; H 8.97.
$C_{15}H_{24}O_4$. Computed %: C 67.13; H 9.01.

Saponifying the addition product. 4 g of the addition product was dissolved in 10 ml of 25% alcoholic caustic potash and then heated for 7 hours over a boiling water bath. The solution was diluted with water, acidulated with dilute sulfuric acid, and extracted with ether. After the ether had been driven off, we had left a thick, noncrystallizing syrup (probably a mixture of the di- and monocarboxylic acids), which was heated to 180° over an oil bath until no more CO_2 was liberated. Distillation of the residue at 160-168° (4 mm) yielded 2.1 g of 2,5,6-trimethyl-Δ^3-cyclohexene-1-carboxylic acid, as a viscous, noncrystallizing syrup. This yielded the amide: white silky needles (from dilute methanol) with a b.p. of 183-184°.

0.1380 g substance: 0.3646 g CO_2; 0.1276 g H_2O.
Found %: C 72.05; H 10.34.
$C_{10}H_{17}ON$. Computed %: C 71.81; H 10.25.

3. Condensing Hexadiene with Ethylidene Acetoacetate

16 g of ethylidene acetoacetate, 12 g of hexadiene, and 0.1 g of hydroquinone were heated to 180° for 18 hours in sealed tubes. Repeated vacuum distillation yielded 9.8 g (40%) of the ethyl ester of 2,5,6-trimethyl-1-acetyl-Δ^3-cyclohexene-1-carboxylic acid:

B.p. 115-117° at 4 mm; n_D^{20} 1.4744; d_4^{20} 1.0247. MR_D 65.59.
$C_{14}H_{22}O_3$ F. Computed: MR_D 65.85.

A colorless, oily liquid with the odor of turpentine.

0.1335 g substance: 0.3440 g CO_2; 0.1120 g H_2O.
Found %: C 70.28; H 9.39.
$C_{14}H_{22}O_3$. Computed %: C 70.55; H 9.30.

Saponification of 4 g of the addition product was effected by heating it with 10 ml of a 25% alcoholic solution of caustic potash for 5 hours over a boiling water bath. The oily liquid that separated out when the reaction mixture was diluted with water was extracted with ether. Driving off the ether and vacuum distillation of the residue yielded 1.5 g (55%) of 2,5,6-trimethyl-1-acetyl-Δ^3-cyclohexene with a b.p. of 115-118° at 22 mm; n_D^{20} 1.4651. The semicarbazone, prepared by the Zelinsky method, was recrystallized from methanol; its m.p. was 165-167°.

0.1036 g substance: 0.2456 g CO_2; 0.0876 g H_2O.
Found %: C 64.65; H 9.46.
$C_{12}H_{21}ON_3$. Computed %: C 64.54; H 9.48.

4. Condensing Hexadiene with Benzal Acetoacetate

12 g of benzal acetoacetate, 8 g of hexadiene, and 0.1 g of hydroquinone were heated to 180° for 20 hours in a sealed tube. This yielded 6.5 g (40%, based on the benzal acetoacetate) of the ethyl ester of 2,5-dimethyl-6-phenyl-1-acetyl-Δ^3-cyclohexene-1-carboxylic acid: B.p. 163-165° at 3 mm; n_D^{20} 1.5309; d_4^{20} 1.0866. MR_D 85.52. $C_{19}H_{24}O_3$. Computed: MR_D 85.34. A thick syrup with high refracting power.

0.1038 g substance: 28.76 g CO_2; 0.0736 g H_2O.
Found %: C 75.57; H 7.93.
$C_{19}H_{24}O_3$. Computed %: C 75.97; H 8.05.

5. Condensing Hexadiene with Benzal Malonate

25 g of benzal malonate, 16 g of hexadiene, and 0.1 g of hydroquinone were heated to 180° in sealed tubes for 12 hours. Repeated distillation succeeded in isolating 9.8 g (30%, based on the benzal malonate) of the diethyl ester of 2,5-dimethyl-6-phenyl-Δ^3-cyclohexene-1,1-dicarboxylic acid:

b.p. 176-180° at 4 mm; n_D^{20} 1.5231; d_4^{20} 1.0945; MR_D 91.62.
$C_{20}H_{26}O_4$. Computed: MR_D 92.23.

A thick oil with a high refractive index.

0.1644 g substance: 0.4363 g CO_2; 0.1159 g H_2O.
Found %: C 72.38; H 7.89.
$C_{20}H_{26}O_4$. Computed %: C 72.70; H 7.93.

SUMMARY

1. The addition products of the diene synthesis with hexadiene of acrylic nitrile, ethylidene malonate and acetoacetate, and benzylidene malonate and acetoacetate have been synthesized.

2. It has been shown that hexadiene-2,4 is a less active diene in a diene synthesis that is piperylidene.

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*See CB translation p. 881 ff.

THE SIGNIFICANCE OF THE STRUCTURE AND POLARITY OF SULFANILAMIDES FOR THEIR BACTERIOSTATIC ACTIVITY

V. THE RELATIONSHIP BETWEEN THE STRUCTURE AND THE BACTERIOSTATIC ACTIVITY OF SULFANILAMIDE COMPOUNDS

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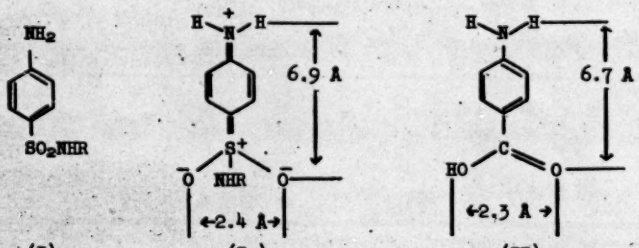
In the preceding paper of this series [1], Z.V.Pushkareva and Z.Yu.Kokoshko demonstrated the importance of certain so-called polar resonance structures of sulfanilamide compounds (I) for their bacteriostatic activity in vitro. The authors attach special importance to "paraquinoid resonance structures" (Ia) with quadrivalent, positively charged atoms of nitrogen in an amino group arranged in a plane.



(I) (Ia) (II)

We assume that the term "paraquinoid resonance structure" has a physical meaning only when interpreted as follows: when the benzene molecule has a NH_2 substituent in it, the molecule is polarized, with the electron density increase at the ortho and para positions. When the benzene molecule contains a SO_2NH_2 group, the polarization of the molecule results in a decrease in the electron density at those positions.

When both of these substituents are introduced into the benzene molecule simultaneously at the para position, the polarization of the molecule also increases from I to Ia at the expense of the reciprocal influence of the substituents on each other. This is borne out by measurements of the dipole moment of sulfanilamide [7]. The addition of the group R to the sulfamide group of sulfanilamide increases or diminishes the total polarization of the molecule, depending upon the nature of R.

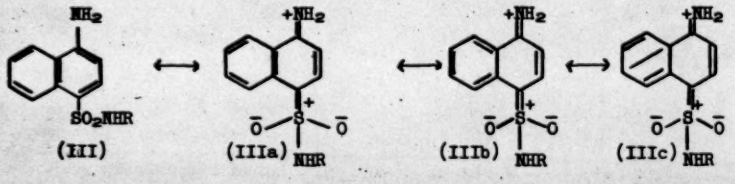
Z.V.Pushkareva and Z. Yu..Kokoshko chose as the numerical values characterizing this polarization of the sulfanilamides the portion of the total mesomerism

energy of these compounds that is manifested only when both substituents are introduced into the benzene molecule simultaneously. They defined this portion of the mesomerism energy as the energy of the para link of the substituents and called it the "excess resonance energy".

In the conclusions of their paper, the authors conclude that it is this polarization of the sulfanilamides that determines their relation to the structurally related p-aminobenzoic acid (II). The latter is an indispensable growth substance, a vitamin, for bacteria, whereas the sulfanilamides are regarded as growth inhibitors, as antivitamins [3], which compete, we may assume, with the p-aminobenzoic acid for possession of certain sections of the substrate in the complex process of formation of bacterial ferment systems.

We assume that the specific polarity of both partners – the vitamin and the antivitamin – actually plays a certain part in this competition, but that the similarity in the dimensions and forms of the molecules of these compounds is decisive.

It is conceivable that even when the structural diagram of the sulfanilamides is distorted, as, say, in the naphthalene sulfamides (III), their molecules will be considerably polarized into paraquinoid structures (IIIa), as was the case with the sulfanilamides (I and Ia). This type of polarization is reinforced by the mesomeric effect of the second naphthalene ring.



When such sulfamides compete with p-aminobenzoic acid, it ought to be harder for them to "fit into the matrix" occupied by the p-aminobenzoic acid in the albumen substrate during the formation of the growth ferments, and hence they cannot exhibit bacteriostatic activity even when their molecules are highly polarized into paraquinoid structures.

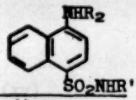
To check the correctness of these hypotheses, which are of fundamental importance to the theory of the links between the structure and the bacteriostatic activity of the sulfanilamides, we synthesized several naphthalene analogs of the active sulfanilamides (Table 1, Nos. 2, 4, 6, and 8) and investigated their bacteriostatic activity. We also determined the mesomerism energy of the compounds 2, 4, and 8 from the heats of combustion of these compounds.

By experimentally determining the heats of combustion of the sulfamides 2,4, and 8 (Table 1), and computing their molecular heats of combustion (W), heats of formation (Q), and energies of formation ($E_{form.}$), we then found the energies of the para bonds ($E_{p\text{-bond}}$), from which the mesomeric effect of the naphthalene ring itself is excluded. These energies thus define the mesomeric effect produced by the simultaneous presence of both substituents at the para position.

Such a method of measuring and computing energies had already been proposed by Z.V.Pushkareva and Z. Yu. Kokoshko [1] and employed by us for determining the so-called "excess resonance energy" of the sulfanilamides. This enabled us

TABLE 1

Aminosulfamides of the Naphthalene Series



No.	R'	R_2	melting point	Per cent nitrogen	
				Computed	Found
1	-H	$-COCH_3$	247-248°	10.61	10.56, 10.73
2	-H	-H	212-213	12.61	12.64, 12.81
3		$-COCH_3$	275-276	12.32	12.38, 12.52
4		-H	231-233	14.04	14.06, 13.99
5		$-COCH_3$	273-274	12.10	12.04, 12.13
6		-H	250-252	13.77	13.68, 13.79
7		$-COCH_3$	252-253	8.95	8.91, 9.10
8		-H	211	9.83	9.73, 9.80

to compare our results with those obtained by the above-mentioned authors (Table 3).

This method required the determination of the mesomerism energies of "deamidized" sulfamides (IV), for which we synthesized the respective substances, listed in Table 2. We also measured the experimental heats of combustion of these substances and computed their heats of formation, energies of formation, and mesomerism energy.

Tests of the antibacterial action of the naphthalene sulfamides in vitro indicated that they possessed almost no activity toward streptococci and staphylococci. This was true even of the analogs of sulfapyridine and sulfathiazole, while testing them in vivo on a typhoid fever culture, Ty2l203, a dysentery culture Flex. 644, and a brucellosis culture of Br. suis yielded the same results.* This agrees with data cited by V.G.Drobotko and associates [4] for their tests of naphthonamide on brucellosis.

These results confirmed our concepts on the significance of the structural outline of the sulfanilamides for their antibacterial activity: despite the considerable magnitude of the para-bond energies of these compounds, which are very close to the analogous values for the sulfanilamides (I) (Table 3), these compounds possess little antibacterial activity.

Thus, the slight antibacterial activity of the naphthalene sulfamides is

*We wish to express our gratitude to Prof. A. I. Pines (All-Union Research Institute of Pharmaceutical Chemistry), Assistant I.D. Zherebtsov (Sverdlovsk Institute of Medicine), and Scientific Worker Schnodieman (Sverdlovsk Institute of Microbiology and Epidemiology) for having tested the activity of the sulfamides.

TABLE 2

Naphthalene Sulfamides (IV)

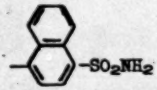
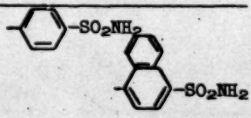
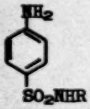
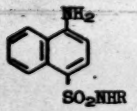
No.	R	Melting point	Per cent nitrogen	
			Computed	Experimental
1	-H	149-150°	6.76	6.97
2		214-215	9.85	9.85 10.07
3		229-230	6.60	6.41, 6.78

TABLE 3

Comparison of the Para-Bond Energies of Some Sulfanilamides and Their Naphthalene Analogs

General sulfamide formula	Para-Bond Energies in Cal/mol for R =		
	-H		
	3.2	15.2	29.1
	2.8	13.8	28.6

combined with high specific polarity of their molecules, which is so fundamental in the series of the active benzene analogs. This bears out the supposition advanced at the outset: that the high bacteriostatic activity of the sulfanilamides, as the result of their competition with p-aminobenzoic acid, is not the result solely of a certain nature of the polarity of sulfanilamide molecules or solely of the resemblance of their structural outline to that of p-aminobenzoic acid, but depends upon the conjunction of these properties, which we propose to term henceforth the "molecular architecture," in which the dimensions and the forms of the molecules themselves play an especially important part.

EXPERIMENTAL

1. Synthesis of naphthalenic sulfamides. The sulfamides of the naphthalene series, listed in Table 1, are not described in the literature, except for the

simplest ones, which have no N'-substituent (Nos. 1 and 2). We prepared the amide of naphthionic acid (2) by the method described by Goldyrev and Postovsky [5], with this sole difference: that the acid chloride of acetylnaphthionic acid was amidated with 25% aqueous ammonia at 50-60° for half an hour instead of with gaseous ammonia.

The N-substituted naphthionamides were prepared by methods resembling those employed for the syntheses of the sulfanilamides: condensing the acid chloride of acetylnaphthionic acid with the corresponding amides in pyridine, and then saponifying the product with a 5% solution of caustic soda. Using more highly concentrated alkali solutions results in the saponification of the condensation products at their sulfamide group.

The "deaminated" sulfamides listed in Table 3 were synthesized similarly, starting with pure α-naphthalenesulfonic acid. Here, too, only the simplest representative of this group, α-naphthylsulfamide, has been described in the literature.

2. Determining the heats of combustion and computing the mesomerism energies of the naphthalene sulfamides. The mesomerism energies of the naphthalene sulfamides were computed by comparing the energies of formation of the molecules of their atomic gases with the aggregate energy of the covalent bonds contained in the molecule. The heats of combustion of the sulfamides, measured experimentally by burning the sulfamides in a platinum bomb calorimeter of ordinary design under standard conditions at 17.5-18.5°, served as the initial data for our calculations of the energies of formation. The heat of combustion was taken as the mean of the results of 4-5 parallel firings, with their results differing by from 1 to 12 cal per gram of substance. As the mean values of the heats of combustion of the sulfamides range from 5300 to 5700 cal/gram, the error involved is ±0.02-0.11%.

The experimental values of the energies of formation were measured in the usual manner, the following values being taken for the heats of formation of gaseous molecules consisting of gaseous atoms: H_2 – 102.6; O_2 – 117.3; and N_2 – 170.2, while the heat of sublimation of a diamond was taken as 125 [6]. In our subsequent computations, we employed the values given by Ya.K.Syrkin [6] for the energies of the various bonds and groups. The energy of the mesomeric effect, which occurs because of the redistribution of the electrons along the lines of the ultimate polar paraquinoid structure and at the expense of the electron interaction of the para substituents, previously proposed by Pushkareva and Kokoshko as a characteristic of the antibacterial activity of the sulfanilamides, was the principal object of our measurements and computations (Table 4).

The method of determing the para-bond energies* ($E_{p\text{-bond}}$) is based on the joint examination of three types of molecules:

"Naphthionamide" (n.a.)

"Deaminated naphthionamide" (de. n. a)

α-Naphthalenesulfamide (n. s.a.)

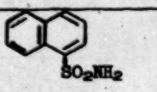
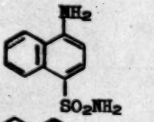
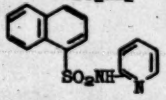
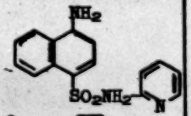
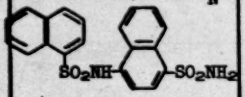
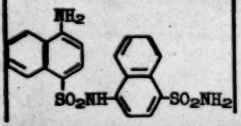
The energies of the mesomeric effect ($E_{m.e.}$) of the N-substituent on the sulfamide group in the deaminated sulfamide were calculated from Equation (1):

$$E_{m.e.SO_2NHR} = E_{form.\ de.n.a.} - E_{form.\ n.s.a.} - E_{form.R} - E_{N-C} + E_{N-H} + E_{C-H} \quad (1)$$

*Cf the paper by Pushkareva and Kokoshko [1] for a detailed explanation of the method of computing excess resonance energies.

TABLE 4

Para-Bond Energies of Sulfamides of the Naphthalene Series and Experimental Data for Computing Them

No.	Sulfamide formulas	Mean heat of combustion, cal/g of substance	Molecular heat of combustion, W, in cal/mol	Heat of formation, Q, Cal/mol	Energy of formation, $E_{form.}$ Cal/mol	Para-bond Energy, $E_{p\text{-}bond}$, Cal/mol
1		6053	1270.8	73.4	1998.5	–
2		5778	1300.6	77.8	2139.3	2.3
3		6572	1884.6	34.5	2823.6	–
4		6303	1902.9	50.3	2975.8	13.8
5		5997	2488.8	131.2	3878.8	–
6		5793	2492.4	161.9	4045.9	28.6

while the para-bond energies were calculated from Equation (2):

$$E_{p\text{-}bond} = E_{form.\ n.a.} - E_{form.\ de.\ n.\ a.} - \underbrace{E_{C-NH_2} + E_{C-H}}_{\text{from } \alpha\text{-naphthylamine}} \qquad (2)$$

SUMMARY

1. A number of naphthalene analogs of active sulfanilamides (Table 1) and the corresponding deaminated compounds (Table 3) have been synthesized for a study of the significance of the structure and the polarity of the sulfanilamides for their bacteriostatic activity.

2. The heats of combustion of these substances have been measured, their heats of formation and their energies of formation have been computed, and the para-bond energies that are characteristic of the polarization of these molecules

toward a limiting polar paraquinoid structure (III → IIIa) have also been determined.

3. It has been found that these energies of the naphthalene sulfamides are very close to those of the analogous active sulfamides (Table 2).

4. Determination of the antibacterial action of sulfamides of the naphthalene series in vitro and in vivo have disclosed their inactivity toward various kinds of bacteria.

5. The hypothesis is advanced that polarization along the lines of paraquinoid structures is a necessary, though not sufficient, condition for the manifestation of antibacterial activity by the sulfanilamides.

The results of the present research indicate that the high bacteriostatic activity of the sulfanilamides, as the result of their competition with p-aminobenzoic acid, is not due solely to the specific nature of the polarity of sulfanilamide molecules or solely to the resemblance of their structural diagram to that of para aminobenzoic acid, but depends, rather, on the conjunction of these properties, i.e., on the "molecular architecture" of the sulfanilamides, the resemblance of the dimensions and forms of their molecules being particularly important.

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